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(54) Title: LOW-HAZE IONOMERS OF COPOLYMERS OF ALPHA-OLEFINS, CARBOXYLIC ACID ESTERS, AND OPTIONAL COMONOMERS, AND PROCESSES FOR MAKING AND ACIDIFYING THESE IONOMERS (57) Abstract Ionomer compositions which have improved optical properties are disclosed. These compositions comprise ionomers which can be represented as the polymerization product of alpha-olefins having from two to eight carbon atoms, esters of alpha, beta-ethylenically-unsaturated carboxylic acids, metal salts of acrylic and methacrylic acid, and optional alpha, beta-ethylenically-unsaturated comonomers which impart some desired polymer property or properties, such as acidity and/or solvent resistivity. Also disclosed are methods of making these ionomer compositions in a reactive extruder and treating the compositions with acid to impart acidity to the compositions or to only the surface of the compositions.		

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1 **LOW-HAZE IONOMERS OF COPOLYMERS OF ALPHA-OLEFINS, CARBOXYLIC**
2 **ACID ESTERS, AND OPTIONAL COMONOMERS, AND PROCESSES FOR**
3 **MAKING AND ACIDIFYING THESE IONOMERS**

4 This application is a continuation-in-part application of
5 U.S. Ser. No. 08/330,290, filed Oct. 27, 1994, which is a
6 continuation-in-part application of U.S. Ser. No.
7 08/144,173, filed Oct. 27, 1993.

8 **BACKGROUND**

9 This invention provides new polymeric ionomer compositions
10 which have low haze. Low haze makes the compositions
11 especially suited for use in clear packaging films, in
12 addition to the other applications in which ionomers are
13 utilized. This invention also provides a method for making
14 these new polymeric compositions and for modifying the
15 acidity of the compositions.

16 The compositions comprise ionomers which can be represented
17 as the polymerization product of alpha-olefins having from
18 two to eight carbon atoms, esters of alpha, beta-
19 ethylenically-unsaturated carboxylic acids, metal salts of
20 acrylic and methacrylic acid, and optional alpha, beta-
21 ethylenically-unsaturated comonomers which impart some
22 desired polymer property or properties, such as acidity
23 and/or solvent resistivity. These ionomer compositions can
24 easily be formed into films.

25 Ionomers which can be formed into films and methods of
26 making ionomers are known in the art. Although these
27 previously-known ionomers have similar chemical constituents
28 to the ionomer compositions of this invention, the known
29 ionomers have significantly different properties from the
30 compositions of this invention. In addition, the known

1 processes for making ionomers are also quite different from
2 the method of making compositions of the present invention.

3 Japanese patent number Sho 49-31556 to Iwami et al., dated
4 Aug. 22, 1974, discloses a process for making ionomers which
5 comprises saponifying copolymers of ethylene and alpha,
6 beta-ethylenically-unsaturated carboxylate esters with a
7 basic metal compound in aliphatic alcohol or in an organic
8 solvent containing an aliphatic alcohol. The copolymer is
9 homogeneously or heterogeneously dispersed in the alcohol
10 solution. The saponified product can be further acidified
11 to provide a composition having acid groups. Although the
12 ionomers which have acid functionality are said to have low
13 haze, no haze values are provided for ionomers which have no
14 acid functionality.

15 Japanese patent number Sho 53-134591 to Harada et al., dated
16 Nov. 24, 1978, discloses a film made by the process of Sho
17 49-31556 which is said to be useful for stretch-wrap
18 applications. Their ionomer comprises a copolymer having
19 90-98 mole percent ethylene, 9.7 to 2.0 mole percent of an
20 alkyl ester of an unsaturated carboxylic acid, 0 to 2.5 mole
21 percent of unsaturated carboxylic acid, and 0.3 to 2.5 mole
22 percent of a metal salt of an unsaturated carboxylic acid.
23 It is stated that their film has very good mechanical,
24 thermal, and optical properties, but the film is limited to
25 having less than 9.7 mole percent ester to prevent blocking
26 occurs between film layers. In addition, the copolymer is
27 limited to a maximum of 2.5 mole percent metal salt of an
28 unsaturated carboxylic acid above which the viscosity of the
29 copolymer is too high to allow processing of the copolymer.
30 All copolymers in the films of the examples contain an
31 unsaturated carboxylic acid component, which, the patent
32 states, is used to adjust the modulus of elasticity and
33 transparency of the film.

1 U.S. patent number 5,218,057, issued to V. Kurkov and
2 L. Theard on June 8, 1993 and which is incorporated by
3 reference in its entirety, teaches a process for saponifying
4 an ethylene alkyl acrylate copolymer which comprises adding
5 an aqueous solution of an inorganic alkali metal base to a
6 molten ethylene-alkyl acrylate copolymer and mixing the
7 alkali metal base and copolymer at a temperature sufficient
8 for saponification to take place and at which the ethylene-
9 alkyl acrylate copolymer remains in a molten or fluid state.
10 Copolymers made by this process have lower tensile strength,
11 lower gloss, and much higher haze than the copolymers of the
12 present invention.

13 U.S. patent number 4,638,034 to McClain, dated Jan. 20, 1987
14 and which is incorporated by reference in its entirety,
15 claims a process for preparing an ethylene-acrylic acid
16 copolymer salt which comprises saponifying an ethylene-alkyl
17 acrylate copolymer in the molten state, in the absence of
18 solvent or water other than by-product alkanol, with alkali
19 metal hydroxide or alkaline earth metal hydroxide under non-
20 static mixing conditions so as to thereby form alkanol and
21 an alkali metal or alkaline earth metal salt of ethylene-
22 acrylic acid copolymer, and separately recovering the
23 alkanol and the salt.

24 U.S. patent number 3,970,626 to Hurst et al., dated July 20,
25 1976, discloses a copolymer of ethylene, alkyl acrylate or
26 methacrylate, and an alkali metal salt of acrylic or
27 methacrylic acid. Although this patent is mainly concerned
28 with forming copolymers which form stable aqueous emulsions,
29 the patent states that the copolymer can be extruded into
30 films of good flexibility. Copolymers in the examples are
31 formed using a batch autoclave. It is stated that about a
32 one-fold excess of sodium hydroxide over what is
33 theoretically required is used to convert the ester groups.

1 U.S. patent number 4,042,766 to Tatsukami et al., dated Aug.
2 16, 1977 and which is incorporated by reference in its
3 entirety, provides a method for preparing ionically cross-
4 linked copolymers comprising melt-blending a copolymer
5 comprising 1) ethylene and 2) at least one alkyl acrylate or
6 methacrylate where the alkyl is selected from the group
7 consisting of isopropyl or tert-butyl, with 3) at least one
8 metal compound selected from the group consisting of
9 acetates, formates, and oxides of zinc, magnesium, calcium,
10 and sodium, and maintaining the molten blend at a
11 temperature of about 200 to 320°C. The patent states that
12 high mixing efficiency is desirable in the reaction
13 equipment to assure uniform dispersion of the metal compound
14 into the ester copolymer and to assure quick evaporation of
15 the low molecular-weight byproducts, such as by melt-
16 blending the components. Per the patent, adequate mixing
17 was provided by a 20 mm-diameter single-screw extruder
18 having a retention time of about one minute, as illustrated
19 in Example 1 of that patent.

20 U.S. patent number 3,789,035 to Iwami et al., dated Jan. 29,
21 1974 and which is incorporated by reference in its entirety,
22 discusses three methods for acidifying an ionomer of a
23 copolymer of ethylene and an ester of an alpha, beta-
24 ethylenically-unsaturated carboxylic acid. The ionomer is
25 made by saponifying a copolymer of ethylene and an ester of
26 an alpha, beta-ethylenically-unsaturated carboxylic acid
27 with a basic metal compound in a solvent containing an
28 alcohol. The patent states that the alcohol is used to
29 promote the reaction of the basic metal compound with the
30 copolymer. The ionomer is then acidified by either 1)
31 adding acid and replacing some of the basic metal with
32 hydrogen; 2) melt-blending a polymer having acid groups with
33 an ionomer; or 3) exchanging a non-alkali metal ion with the

1 alkali metal ion on the ionomer which has been dispersed in
2 a solvent.

3 U.S. patent number 3,264,272 to Rees, dated Aug. 2, 1966,
4 claims a composition comprising a random copolymer of an
5 alpha-olefin having from two to ten carbon atoms, an alpha,
6 beta-ethylenically-unsaturated carboxylic acid having from
7 three to eight carbon atoms in which 10 to 90 percent of the
8 acid is neutralized with metal ions, and an optional third
9 mono-ethylenically unsaturated comonomer such as methyl
10 methacrylate or ethyl acrylate. This copolymer is acidic
11 due to the carboxylic acid groups present in the copolymer.
12 U.S. patent number 3,404,134 discloses the process for
13 making these compositions, which comprises reacting an
14 ethylene acrylic acid copolymer with a metal compound at a
15 pressure between 100 and 10,000 psi and a temperature above
16 the melt-point of the copolymer.

17 U.S. patent number 5,189,113 to Muehlenbernd et al., dated
18 Feb. 23, 1993, discloses a process for making ionically
19 cross-linked copolymers of ethylene and alpha, beta-
20 ethylenically-unsaturated carboxylic acids or alpha, beta-
21 ethylenically-unsaturated comonomers donating carboxyl
22 groups, such as anhydrides. This process requires reacting
23 the copolymer with a solid metal compound in a mixing zone
24 of a twin-screw extruder and subsequently pumping in water.
25 The advantages for this process are said to be that no
26 discoloration of the ionomer occurs because no corrosion of
27 the twin-screw extruder occurs, and no specks of unreacted
28 solid metal compound are found in the ionomer film.

29 U.S. patent number 5,003,001 to Hasenbein et al., dated Mar.
30 26, 1991, claims a process for making ionically cross-linked
31 copolymers of ethylene and alpha, beta-ethylenically-
32 unsaturated carboxylic acids or alpha, beta-ethylenically-

1 unsaturated comonomers donating carboxyl groups, such as
2 anhydrides. This process reacts the copolymer with an
3 aqueous metal salt solution in a first reaction zone at a
4 temperature from 140 to 180°C to form ionomer and completely
5 devolatilizes the ionomer in a second, three-stage
6 devolatilization zone at a temperature from 200 to 270°C.
7 This process is said to provide odor-free ionomer film which
8 is free of specks.

9 Although there has been much research in the area of
10 ionomers, what has been lacking in the prior art is
11 optically clear ionomers comprising copolymers of alpha
12 olefins having two to eight carbon atoms, esters of alpha,
13 beta-ethylenically-unsaturated carboxylic acids, and metal
14 salts of alpha, beta-ethylenically-unsaturated carboxylic
15 acids as well as methods of making those ionomers. This
16 invention provides such compositions and methods.

17 SUMMARY OF THE INVENTION

18 In one embodiment, the invention comprises a copolymer of
19 alpha-olefins having from two to eight carbon atoms, esters
20 of alpha, beta-ethylenically-unsaturated carboxylic acids
21 having from four to twenty-two carbon atoms, and metal salts
22 of acrylic or methacrylic acid, wherein this copolymer has a
23 haze of no more than ten percent as measured by ASTM method
24 D 1003.

25 In one preferred embodiment, the invention comprises a
26 copolymer of ethylene, methyl acrylate, and sodium salt of
27 acrylic acid, wherein the haze of the copolymer is no more
28 than five percent.

29 In another embodiment, the invention comprises a method of
30 making an ionomer composition. This method comprises
31 contacting a Group IA metal-containing solution with a

1 molten or fluid copolymer comprising alpha-olefins having
2 from two to eight carbon atoms and esters of alpha, beta-
3 ethylenically-unsaturated carboxylic acids having from four
4 to twenty two carbon atoms and having a melt index between
5 about 100 and about 2000 g/10 min., as measured by ASTM
6 method D 1239 at 190°C using a 2.16 kg weight; and
7 intensively mixing the copolymer and Group IA metal-
8 containing solution at a temperature and to an extent which
9 provides an ionomer composition having no more than ten
10 percent haze.

11 In another embodiment, the invention comprises a method of
12 reducing the water solubility of an ionomer composition
13 formed into a shape such as strands, pellets, or film, which
14 method comprises contacting a surface of the shape with an
15 acid.

16 Among other factors, the present invention is based on our
17 finding that films of the composition as described herein
18 have very low haze, particularly when the films are made
19 after saponifying a copolymer as described above under
20 conditions which include intensive mixing, a greater extent
21 of saponification, and higher reaction temperatures. Film
22 haze is no more than ten percent, and many films have a haze
23 of no more than five or even two percent. Furthermore, in a
24 preferred embodiment, the composition has improved
25 properties such as improved tensile strength, hot tack
26 strength, and/or heat seal strength over ionomers of similar
27 composition.

28 In addition to the properties discussed above, many of the
29 compositions of this invention have no acidity, regardless
30 of the extent of saponification. These advantages and
31 others are further described below.

DESCRIPTION OF THE FIGURES

Figure 1 is a scanning electron micrograph of a freeze-fractured cross-section of 3-mil thick film made from an ionomer composition of this invention, taken at a magnification factor of 8,000.

Figure 2 is a scanning electron micrograph of a freeze-fractured cross-section of 3-mil thick film of ionomer of Comparative Example G. Figure 2 illustrates that spherical and oblong ionic clusters or regions are present in the ionomer. This micrograph was also produced at a magnification factor of 8,000.

A JEOL JSM-820 scanning electron microscope was used to generate the micrographs. The micrographs of Figures 1 and 2 show the fracture surface of films which were made by the blown film process of the examples.

Figure 3 shows the hot-tack of ionomer of this invention from Example 20 as a function of temperature. The ordinate is temperature in °C, and the abscissa is hot-tack, measured in Newtons/inch. Line 1 is 35% hydrolyzed ionomer, line 2 is 42% hydrolyzed ionomer, and line 3 is 50% hydrolyzed ionomer.

Figure 4 shows the heat seal strength of the ionomer/polyethylene film of Example 22 as a function of temperature. The ordinate is temperature in °F and the abscissa is the heat seal strength in lb/inch.

DETAILED DESCRIPTION OF THE INVENTION

A. Compositions

Compositions of this invention can be represented as the copolymerization product which contains the following comonomers:

- 1 (a) alpha-olefins having from 2 to 8 carbon atoms,
- 2 (b) esters of alpha,beta-ethylenically-unsaturated
- 3 carboxylic acids,
- 4 (c) metal salts of acrylic or methacrylic acid, and
- 5 (d) optionally, other alpha, beta-ethylenically-unsaturated
- 6 comonomers which impart desirable polymer properties.

7 These compositions have no more than ten percent haze,
8 preferably no more than seven percent haze, and more
9 preferably, no more than five percent haze. The most
10 preferred compositions have no more than two percent haze.
11 Additionally, these compositions have very good hot tack
12 strength, heat seal strength, and mechanical properties such
13 as tensile strength. Acid functionality can also be
14 introduced into these ionomers.

15 Examples of compositions of this invention include ethylene-
16 methyl acrylate-sodium acrylate ionomer, ethylene-methyl
17 methacrylate-sodium methacrylate ionomer, ethylene-ethyl
18 acrylate-sodium acrylate ionomer, ethylene-propylene-methyl
19 acrylate-sodium acrylate ionomer, ethylene-propylene-methyl
20 methacrylate-sodium methacrylate ionomer, ethylene-methyl
21 acrylate-lithium acrylate ionomer, ethylene-methyl acrylate-
22 potassium acrylate ionomer, ethylene-methyl acrylate-
23 cobalt(II) or (III) acrylate ionomer, ethylene-methyl
24 acrylate-zinc acrylate ionomer, ethylene-methyl acrylate-
25 titanium(II), (III), or (IV) acrylate ionomer, ethylene-
26 methyl acrylate-magnesium acrylate ionomer, ethylene-methyl
27 acrylate-iron(II) or (III) acrylate ionomer, ethylene-methyl
28 acrylate-nickel(II) or (III) acrylate ionomer, ethylene-
29 methyl acrylate-copper(I) or (II) acrylate ionomer,
30 ethylene-methyl acrylate-acrylic acid-sodium acrylate

1 ionomer, ethylene-methyl methacrylate-methacrylic acid-
2 sodium methacrylate ionomer, ethylene-methyl acrylate-sodium
3 acrylate ionomer grafted with maleic anhydride, ethylene-
4 methyl acrylate-maleic anhydride-sodium acrylate ionomer,
5 and acrylic acid-grafted-(ethylene-methyl acrylate-sodium
6 acrylate) ionomer.

7 Monomer (a) comprises alpha-olefins having from 2 to 8
8 carbon atoms. Preferably, monomer (a) comprises alpha-
9 olefins having from 2 to 3 carbon atoms, and more
10 preferably, monomer (a) consists essentially of ethylene.

11 Monomer (b) comprises esters of alpha, beta-ethylenically-
12 unsaturated carboxylic acids having from 4 to 22 carbon
13 atoms. Preferably, monomer (b) has from 4 to 13 carbon
14 atoms, and more preferably has from 4 to 8 carbon atoms.
15 Examples of monomer (b) include methyl acrylate, methyl
16 methacrylate, ethyl acrylate, ethyl methacrylate, butyl
17 acrylate, and butyl methacrylate. Methyl acrylate is the
18 preferred monomer (b).

19 Monomer (c) is a metal salt of acrylic or methacrylic acid.
20 The metal ion is selected from Group IA, Group IIA, and
21 transition metal ions. The metal ions may also be aluminum,
22 gallium, germanium, and tin. Other examples include
23 lithium, sodium, potassium, rubidium, cesium, calcium,
24 magnesium, zinc, titanium, iron, cobalt, nickel, and copper.
25 Preferably, the metal ion is a Group IA or Group IIA metal
26 ion, and more preferably, the metal ion is a Group IA metal
27 ion. Most preferred is sodium. Monomer (c) is about 25 to
28 99 mole percent of the total amount of (b) and (c) present
29 in a composition. Preferably, monomer (c) is about 35 to
30 80, and more preferably, is about 40 to 60, mole percent of
31 the total amount of (b) and (c) present in a composition.

1 Typically, a composition of this invention contains from
2 about 1 to 20 mole percent of monomers (b) and (c) in total.
3 Preferably, a composition contains about 3.5 to 12.5 mole
4 percent, and more preferably, about 5.5 to 10 mole percent
5 of monomers (b) and (c). Most preferred is a composition
6 containing about 7.5 to 10 mole percent of monomers (b) and
7 (c).

8 Monomer (d) is an alpha, beta-ethylenically-unsaturated
9 comonomer which imparts certain desired polymer properties.
10 The amount and type of monomer (d) are determined by the
11 particular properties that are desired in the final
12 composition. For example, monomer (d) may be acrylic or
13 methacrylic acid which is present in an amount that provides
14 the desired acid functionality to the composition. Other
15 examples of monomer (d) include maleic anhydride and maleic
16 acids to impart acidity, acrylonitrile to impart solvent
17 resistance, and styrene to increase the rigidity of the
18 composition. Typically, the compositions contain 0 to 10
19 mole percent of monomer (d). Preferred compositions contain
20 0 to 5 mole percent of monomer (d).

21 Monomer (d) can also be added by grafting a group such as
22 acrylic acid or maleic anhydride to a composition of the
23 present invention or to one of the composition's precursors.
24 As a result, compositions can comprise grafted (ethylene,
25 (meth)acrylate, metal salt of (meth)acrylic acid)
26 copolymers. Maleic anhydride-grafted (ethylene, methyl
27 acrylate, sodium acrylate) copolymer is one such
28 composition.

29 The ionomer compositions of this invention have a number of
30 surprising features which distinguish them from other
31 ionomers having similar chemical constituents. The ionomers
32 of this invention are quite clear. Haze is typically no

1 more than 5 percent. Also, in one preferred embodiment, the
2 60° gloss is typically at least 100, and in many instances,
3 is at least 120. In another preferred embodiment, tensile
4 strength of the composition is improved over ionomers of
5 similar composition by 100-300 percent. Hot-tack strength
6 and heat seal strength can also be improved over ionomers of
7 similar composition. Combinations of these improved
8 features are present in some preferred compositions of this
9 invention.

10 For example, the haze, gloss, and tensile strength of
11 ionomer of this invention are substantially different from
12 the haze, gloss, and tensile strength of ionomer made by the
13 process of U.S. Pat. № 5,218,057. Ethylene-methyl acrylate
14 copolymer having about 20 weight percent (about 7.5 mole
15 percent) methyl acrylate and having about 65% of the methyl
16 acrylate saponified with aqueous sodium hydroxide according
17 to the process of U.S. Pat. № 5,218,057 had a haze of 15%
18 and 60° gloss of 66. Tensile strength of an ethylene-methyl
19 acrylate copolymer having 20 weight percent methyl acrylate
20 which had about 60% of the methyl acrylate groups saponified
21 with aqueous sodium hydroxide according to the process of
22 U.S. Pat. № 5,218,057 was 1582 psi in the machine direction.
23 A composition of the present invention made by saponifying
24 an ethylene-methyl acrylate copolymer having about 20 weight
25 percent methyl acrylate with aqueous sodium hydroxide to
26 convert about 65% of the methyl acrylate groups had a haze
27 of 2%, gloss of 133, and tensile strength in the machine
28 direction of 4010 psi.

29 The ionomers of this invention also can be formed into very
30 thin film. When blowing film, the blow-up ratio can be as
31 high as 2:1 to about 2.5:1. Typically, a film of ionomer of
32 this invention can have a thickness of less than about 1
33 mil. Film having a thickness of about 0.5 mil has been

1 made, and film having a thickness of about 0.2 - 0.3 mil can
2 be made on conventional processing equipment.

3 The morphology of prior art ionomers can also differ
4 substantially from the morphology of ionomers of this
5 invention. Prior-art ionomers can contain highly localized
6 and large clusters of ionic material dispersed throughout
7 the ionomer. Scanning-electron micrographs have shown that
8 these clusters can range in size from about 0.05 micron to
9 greater than 1 micron in size.

10 Figure 2 is a scanning-electron micrograph for the ionomer
11 of Comparative Example G. This ionomer consists essentially
12 of ethylene, 5.7 mole percent methyl acrylate, and 1.8 mole
13 percent of the sodium salt of acrylic acid. The spherical
14 or oblong ionic clusters evident in this micrograph range in
15 size from about 0.1 micron to about 0.5 micron. The
16 clusters were determined to be ionic by energy-dispersive
17 X-ray spectroscopy, which showed a higher sodium content
18 within the clusters when compared to the surrounding
19 continuous phase.

20 Figure 1 is a scanning-electron micrograph for ionomer
21 composition of this invention, which consists essentially of
22 ethylene, 3.7 mole percent methyl acrylate, and 3.7 mole
23 percent of the sodium salt of acrylic acid. This ionomer
24 composition is substantially free of ionic clusters of the
25 size seen in Figure 2, since essentially no ionic clusters
26 are observed in this micrograph. An ionomer composition
27 which is substantially free of ionic clusters contains
28 essentially no ionic clusters about 0.05 micron in size or
29 larger when a freeze-fractured cross-section of 3-mil thick
30 blown film which is made by the method of Example 1 is
31 viewed with a scanning electron microscope at a
32 magnification factor of 8,000. An ionomer composition which

1 is substantially free of ionic clusters will also have a
2 haze of no more than ten percent. The ionomer composition
3 of Figure 1 corresponds to the composition of Example 12,
4 which had a haze of 3%. The large flecks of debris in
5 Figure 1 are believed to be foreign matter. The flecks are
6 not regions having high sodium content.

7 Additives well-known in the art may be included in the
8 ionomer, such as anti-block and slip additives and anti-
9 oxidants. Preferably, the composition of this invention
10 also contains a polymeric acid having a molecular weight of
11 less than about 10,000, such as ethylene acrylic acid.
12 Ionomer compositions containing these low molecular weight
13 acids are disclosed in copending U.S. Ser. No. 08/188,848,
14 filed Jan. 31, 1994, which is incorporated by reference in
15 its entirety herein.

16 B. Method for making the compositions

17 One method for making compositions of this invention
18 comprises saponifying a copolymer having ester groups with a
19 Group IA metal-containing solution. To obtain the clear
20 ionomer compositions of this invention, it is important to
21 provide intensive mixing of the copolymer and the Group IA
22 metal-containing solution and to have a temperature and/or
23 extent of saponification high enough that a substantially
24 uniform saponification of the copolymer occurs. This method
25 minimizes the production of localized ionomer regions or
26 domains, which appear as the spherical and oblong ionic
27 clusters of Figure 2. This method also permits a greater
28 extent of saponification of the copolymer without obtaining
29 a saponified product that has so high of a viscosity that it
30 cannot be formed into a film on conventional equipment.

31 Intensive mixing of the reaction components results from
32 selection of reactants with the appropriate physical and

1 chemical characteristics and selection of the proper
2 processing conditions. Particular processing conditions are
3 discussed below for a reactive extruder. However, the
4 general principles disclosed therein apply to processes
5 which are equivalent to saponifying a copolymer with a
6 Group IA metal-containing solution in a reactive extruder..

7 (1) Reactants

8 (a) Copolymer to be saponified

9 The copolymers which are saponified comprise copolymers of
10 ethylene, esters of alpha, beta-ethylenically-unsaturated
11 carboxylic acids, and optional alpha, beta-ethylenically-
12 unsaturated comonomers which impart desirable polymer
13 properties. Typically, these copolymers contain from about
14 1 to 20 mole percent of esters of alpha, beta-ethylenically-
15 unsaturated carboxylic acids in total. Preferably, the
16 copolymers contain about 2 to 20 mole percent, more
17 preferably 3.5 to 12.5 mole percent, and even more
18 preferably, about 5.5 to 12.5 mole percent of esters of
19 alpha, beta-ethylenically-unsaturated carboxylic acids in
20 total. Most preferred are those copolymers containing about
21 6.5 to 10 mole percent of esters of alpha, beta-
22 ethylenically-unsaturated carboxylic acids. The preferred
23 esters are alkyl acrylates. Preferably, the alkyl group
24 contains from one to eight carbon atoms, and more preferably
25 contains from one to four carbon atoms. Methyl is a
26 preferred alkyl group.

27 Examples of the copolymers which are saponified include
28 ethylene-methyl acrylate copolymer, ethylene-methyl
29 methacrylate copolymer, ethylene-ethyl acrylate copolymer,
30 ethylene-propylene-methyl acrylate copolymer, ethylene-
31 propylene-methyl methacrylate copolymer, ethylene-methyl
32 acrylate-acrylic acid copolymer, ethylene-methyl
33 methacrylate-methacrylic acid copolymer, maleic anhydride-

1 grafted-ethylene-methyl acrylate copolymer, ethylene-methyl
2 acrylate-maleic anhydride copolymer, acrylic acid-grafted-
3 ethylene-methyl acrylate copolymer, and ethylene-methyl
4 acrylate-butyl acrylate copolymer. Preferably, the
5 copolymers are ethylene-methyl acrylate copolymer, ethylene-
6 methyl methacrylate copolymer, ethylene-ethyl acrylate
7 copolymer, maleic anhydride-grafted-ethylene-methyl acrylate
8 copolymer, and ethylene-methyl acrylate-butyl acrylate
9 copolymer. Most preferred is ethylene-methyl acrylate
10 copolymer.

11 The melt index of copolymers to be saponified should be
12 between about 100 and 2000, preferably between about 200 and
13 800, and more preferably between about 300 and 600 grams/10
14 minutes. Copolymers having higher melt-index values are
15 preferred when it is desired to have a saponified
16 composition with a higher melt index. One process for
17 making these copolymers comprises polymerizing ethylene,
18 alkyl acrylate and/or alkyl methacrylate, and the optional
19 comonomer in autoclaves using free-radical initiation
20 catalysts. This process is described in U.S. Patent
21 # 3,350,372, which is incorporated by reference in its
22 entirety. The copolymers of the examples were made by this
23 method, unless specified otherwise. In one preferred
24 embodiment, the ethylene-alkyl acrylate copolymer is made by
25 the process described in copending U.S. Ser. No. 07/947,870,
26 filed Sep. 21, 1992 (published as WO 93/06137), which is
27 incorporated by reference in its entirety herein. Copolymer
28 made by this process has a substantially higher melt-point
29 temperature than the copolymer made by the process of U.S.
30 Patent No. 3,350,372. The ionomer of this invention has
31 high melt point temperature and high clarity when made with
32 this copolymer. Another process for producing copolymers
33 useful in making the ionomer compositions of this invention
34 comprises free-radical polymerization of ethylene and alkyl

1 acrylate and/or alkyl methacrylate as described above,
2 followed by reactive extrusion with a compound such as
3 acrylic acid or maleic anhydride. Alternatively, grafting
4 may be performed after saponification. A particularly
5 preferred copolymer is ethylene-methyl acrylate copolymer
6 having between about 5.5 and 12.5 mole percent methyl
7 acrylate and having a melt index of about 400 g/10 min.,
8 available from Chevron Chemical Company as EMAC® copolymer.

9 (b) Group IA metal-containing solution

10 The Group IA metal-containing solution comprises a Group IA
11 metal in a solvent, which solvent does not prevent
12 saponification of an ester by the Group IA metal. The
13 solvent is preferably one which evaporates readily under
14 devolatilization conditions typically encountered in
15 reactive extruders. Solvents can be organic or inorganic,
16 and common solvents include water, alcohols, and
17 polyethylene glycols, with water being preferred.

18 The Group IA metal-containing solution has at least one
19 Group IA metal present. Preferably, the solution comprises
20 an aqueous solution of a Group IA metal oxide and/or
21 hydroxide, such as oxides and hydroxides of lithium, sodium,
22 potassium, rubidium, and/or cesium. Preferably, the
23 Group IA metal-containing solution comprises aqueous sodium
24 hydroxide or aqueous potassium hydroxide.

25 It is important that the overall concentration of metals in
26 the Group IA metal-containing solution is low enough that
27 the solution is capable of being mixed uniformly and
28 intensively with melted copolymer in a reaction section of a
29 reactive extruder. However, it is preferred to have only
30 that amount of solvent present that is necessary to provide
31 this capability. Normally, a sufficient quantity of solvent
32 is present when the Group IA metal-containing solution

1 contains little or no excess solvent beyond that required to
2 solubilize essentially all of the Group IA metal and other
3 metals present. Thus, for example, 50% aqueous caustic
4 solution is preferred over 35% aqueous caustic solution.

5 The Group IA metal-containing solution may optionally
6 contain other metal oxides, hydroxides, and/or salts which
7 supply cations for monomer (c). The metal ions can be
8 alkaline earth or transition-element metals. Specific
9 examples of these metals include calcium, magnesium, zinc,
10 titanium, cobalt, nickel, and copper. Typical anions
11 include hydroxide, halide, acetate, propionate, decanoate,
12 and stearate ions, with acetate ions being preferred anions.
13 The hydroxide form is also preferred.

14 Instead of being present in the Group IA metal-containing
15 solution, metal ions (including Group IA metal ions) may
16 optionally be incorporated into the ionomer composition of
17 this invention by other methods. One method is to first
18 saponify a copolymer by the method of this invention, then
19 totally or partially replace the ion of this ionomer
20 composition with other metal ions under ion-exchange
21 conditions, or to react the ionomer composition with an
22 aqueous metal hydroxide. For example, an ion-exchange
23 solution comprising an aqueous solution of zinc oxide or
24 zinc acetate may be mixed with a sodium ionomer composition
25 of this invention in a section of a reactive extruder to
26 replace at least a portion of the sodium ions with zinc
27 ions.

28 Examples of metal ions which may be exchanged include the
29 alkaline metals, alkaline earth metals such as magnesium,
30 transition metals such as titanium, cobalt, copper, and
31 zinc, and other metal ions such as aluminum, gallium,
32 germanium, and tin.

1 The anion of a salt used to ion-exchange the ionomer is
2 preferably one which is easily washed out of the ionomer and
3 separated from it during filtration. Alternatively, the
4 anion is preferably one which forms an easily-evolved
5 compound or one which evolves or whose products of
6 decomposition evolve at devolatilization conditions in a
7 reactive extruder. Typical anions include chloride,
8 acetate, propionate, decanoate, and stearate ions. Acetate
9 ions are preferred.

10 (2) Reactive Extruder

11 A reactive extruder which is useful in producing
12 compositions of this invention comprises an extruder having
13 a copolymer feed section, one or more reaction sections, a
14 subsequent devolatilization section, and an extrusion
15 section. Typically, these sections are separately jacketed
16 to allow for heating or cooling within each section. These
17 sections can also be vented with one or more vent ports per
18 section to allow the escape of volatile components, such as
19 the solvent for the Group IA metal solution and byproducts
20 of the saponification reaction, such as alcohols.
21 Generally, the reactive extruder will also have optional
22 means for introducing reactants into any reaction sections
23 as well as means for mixing components in the reaction
24 section(s) and means for conveying the components through
25 the extruder. Typically, the means for mixing and conveying
26 components to be reacted are screws.

27 Reactive extruders can have a single screw or multiple
28 screws. Each screw typically has a central shaft with a
29 key-way or spline upon which mixing elements are secured.
30 The reactive extruder may have either co-rotating or
31 counter-rotating screws.

1 Typically, copolymer to be reacted is fed to the screw
2 through a loss-in-weight feeder, and the solid copolymer is
3 melted in a feed section of the reactive extruder. In some
4 embodiments, all reactants (i.e. copolymer and Group IA
5 metal-containing solution) can be fed to the reactive
6 extruder through a feed section. In a preferred embodiment,
7 copolymer is introduced into the reactive extruder in a feed
8 section, and the Group IA metal-containing solution is fed
9 to one or more reaction sections. A devolatilization
10 section is a convenient means for removing any solvent and
11 byproducts of the saponification reaction from the
12 saponified composition. Equivalent or additional means for
13 removing volatile components can be used, however, such as
14 drying the ionomer composition under reduced pressure in a
15 falling-film evaporator.

16 One reactive extruder which was particularly effective in
17 producing compositions of this invention is a Werner-
18 Pfleiderer co-rotating and intermeshing twin-screw extruder.
19 The reactive extruder had a feed section, a reaction
20 section, a devolatilization section, and a pressurization or
21 pumping section which pushed the product through an
22 extrusion die. The devolatilization section had a first
23 portion which was vented to a condenser maintained at
24 atmospheric pressure, and a second portion of the
25 devolatilization section was vented with sufficient vacuum
26 and capacity to remove essentially all of the volatile
27 components from compositions prior to conveying and
28 extruding them.

29 Typically, copolymer pellets are introduced into a feed
30 section of a reactive extruder, where the pellets are heated
31 and worked by the screw to form molten or fluid copolymer.
32 The screw elements also convey the molten copolymer from
33 this feed section to a first reaction section, where the

1 molten copolymer and Group IA metal-containing solution are
2 mixed intensively.

3 Intensive mixing can be supplied by incorporating one or
4 more reverse-flow elements along with neutral or reverse-
5 flow kneading blocks on the screw in a reaction zone. The
6 copolymer to be saponified and the Group IA metal-containing
7 solution should be mixed as uniformly and as quickly as
8 possible to provide a fairly uniform reaction of metal-
9 containing solution with the molten copolymer. Mixing
10 should be of sufficient intensity that saponification of
11 only localized areas is prevented.

12 This intensive mixing is of greater intensity than that
13 required in the prior-art processes of U.S. Pat. № 4,638,034
14 and U.S. Pat. № 4,042,766. For example, a Werner-Pfleiderer
15 Model ZSK-40 twin-screw reactive extruder had the
16 configuration of screw elements detailed in Table 1 column
17 A. This screw design provided intensive mixing of the
18 Group IA metal-containing solution with copolymer in the
19 reaction section through a combination of left-handed
20 elements and neutral kneading blocks. It is believed that
21 the left-handed elements in the reaction section provide
22 momentary retardation of polymer flow in addition to a shear
23 zone due to impeded and/or reversed flow of the reaction
24 mass, while the neutral kneading blocks imparted intensive
25 mixing and promoted additional shear. Most of the
26 compositions of this invention were produced at a screw
27 speed of about 400 to 550 rpm. High screw speeds help to
28 assure intensive mixing.

TABLE 1

ELEMENT NUMBER	COLUMN A	COLUMN B	COLUMN C
1	40/20 ¹	PKR/10 ²	PKR/10
2	60/60	20/10	20/10

	ELEMENT NUMBER	COLUMN A	COLUMN B	COLUMN C
1	3	60/60	42/42	42/42
2	4	40/40	42/42	42/42
3	5	40/40	42/42	28/28
4	6	40/40	28/28	28/28
5	7	40/20	28/28	28/28
6	8	40/40	20/20	20/20
7	9	25/25	20/20	20/20
8	10	KB45/5/40 ³	20/20	20/20
9	11	KB45/5/40	KB45/5/28	20/10
10	12	25/25	KB45/5/28	KB45/5/28
11	13	25/25	20/20	KB45/5/28
12	14	25/25	20/20	20/20
13	15	40/20 LH ⁴	KB90/5/28	20/20
14	16	25/25	20/10 LH	20/10 LH
15	17	KB90/5/40	20/20	20/10 LH
16	18	25/25	20/20	20/10 LH
17	19	KB90/5/40	KB45/5/28	20/20
18	20	25/25	20/10	20/20
19	21	40/20 LH	20/20	KB45/5/28
20	22	25/25	20/20	20/10
21	23	KB90/5/40	KB90/5/28	20/20
22	24	25/25	20/20	20/20
23	25	KB90/5/40	KB45/5/14 LH	KB90/5/28
24	26	25/25	KB45/5/14 LH	20/20
25	27	40/20 LH	20/20	KB45/5/14 LH
26	28	KB45/5/20 LH	20/20	KB45/5/14 LH
27	29	25/25	KB90/5/28	20/20
28	30	25/25	20/20	20/20
29	31	25/25	20/20	KB90/5/28
30	32	25/25	20/20	20/20
31	33	25/25	20/20	20/20
32	34	40/40	20/20	20/20
33	35	40/40	KB90/5/28	20/20
34	36	40/40	20/20	KB90/5/28
35	37	KB45/5/20 LH	20/20	20/20
36	38	40/40	20/20	20/20
37	39	40/40	20/20	20/20
38	40	40/40	20/20	20/20
39	41	40/40	20/20	KB90/5/28
40	42	25/25	20/20	20/20
41	43	25/25	20/20	20/20
42	44	25/25	KB90/5/28	20/10
43	45	25/25	20/20	20/20
44	46	25/25	20/20	20/20
45	47	25/25	20/10 LH	20/20
46	48	25/25	20/10 LH	20/20
47	49	25/25	20/20	20/20
48	50	25/25	20/20	20/20
49	51	25/25	20/20	20/20
50	52	25/25	20/20	20/20

	ELEMENT NUMBER	COLUMN A	COLUMN B	COLUMN C
1	53	25/25	42/42	20/20
2	54	25/25	42/42	20/20
3	55	25/25	42/42	42/42
4	56		20/20	42/42
5	57		20/20	42/42
6	58		20/20	28/28
7	59		20/20	20/20
8	60		20/20	20/20
9	61			20/20

NOTES:

1. All elements were right-handed elements unless designated otherwise. The first number is the pitch, given in distance (mm) traveled in one revolution. The second number is the length of the element (mm).
2. The PKR element is a wedge-shaped adapter which provides a taper from the 1/2 inch shaft to the first element of the screw.
3. KB indicates a kneading block. The first number is the angle formed by the paddles on the kneading block when compared to the line through the screw shaft, in degrees. The second number is how many paddles are on one element. The third number is the length of the element (mm).
4. "LH" indicates a left-handed element.

(3) Reaction conditions

Reaction temperature, feed-rate of reactants, and extent of saponification are also important processing parameters when making compositions of this invention.

(a) Reaction temperature

Compositions of this invention are typically produced where the barrel temperature in the reaction section(s) of the extruder is between about 200 and 350°C, although some clear ionomers were prepared at a temperature between about 150 and 200°C. Any reaction temperatures discussed herein refer

1 to the barrel temperatures of the extruder. The actual
2 temperature of the melted polymer is believed to be lower
3 than the measured barrel temperature because of heat-
4 transfer limitations.

5 Preferably, the reaction temperature is between 225 and
6 350°C, and, more preferably, the temperature is between
7 about 275 and 350°C. The upper limit of the temperature
8 range is determined by the temperature at which the
9 copolymer or composition degrades. The lower limit of the
10 temperature range is the temperature at which 1) the
11 copolymer to be reacted is in a molten or fluid state;
12 2) essentially all of the Group IA metal in the Group IA
13 metal-containing solution is consumed by the saponification
14 reaction within the reaction section; and 3) the composition
15 being extruded remains visually clear. As a general rule,
16 higher reaction temperatures as specified in the more
17 preferable range above provide low-haze ionomers more
18 consistently than lower reaction temperatures.

19 (b) Feed rate of reactants

20 The Group IA metal-containing solution is fed in an amount
21 that is effective to achieve the desired extent of
22 saponification of the copolymer being fed to the reactive
23 extruder. Typically, essentially all of the Group IA metal
24 in solution reacts with the copolymer. The Group IA metal-
25 containing solution may be fed to a reaction section batch-
26 wise or continuously, or it may be fed intermittently so
27 that the solution is mixed intimately and rapidly with the
28 molten copolymer. A continuous feed is preferred. The
29 Group IA metal-containing solution may also be split between
30 multiple reaction sections and be fed continuously and/or
31 intermittently to any reaction section.

1 The copolymer to be saponified is fed to the reactive
2 extruder at a rate high enough that the molten polymer forms
3 a molten polymer seal between consecutive segments of a
4 reaction section and between a reaction section and a
5 devolatilization section. This seal can be formed by having
6 a reverse-flow screw element at the desired seal location.
7 The feed-rate should also be low enough that the reaction
8 mass comprising the copolymer to be saponified and the
9 Group IA metal-containing solution does not move through the
10 reaction section so quickly that the reaction mass is not
11 mixed intensively. The feed-rate should also be low enough
12 that the extruded polymer is visually clear, corresponding
13 to no more than ten percent haze.

14 The copolymer to be saponified may be fed to the extruder
15 batch-wise, intermittently or continuously. A continuous
16 feed is preferred to provide a commercially-attractive
17 process which is easily and effectively controlled.

18 Typically, the average residence time for reactants in a
19 Werner & Pfleiderer ZSK-40 twin-screw extruder which has a
20 feed section, one reaction section, devolatilization
21 section, and pumping section is about 30 to about 40 seconds
22 at a continuous feed-rate of approximately 100 lb./hr. of
23 polymer to be saponified and at a screw speed of about 500
24 rpm. The average residence time in the reaction section of
25 this reactive extruder at these conditions is typically
26 about 5 to about 15 seconds.

27 When the feed-rate is too high to make a composition of this
28 invention, the screw torque will decrease, and the ionomer
29 will turn cloudy. Both of these conditions can be observed
30 almost immediately upon feeding too much copolymer to the
31 extruder. Visually, the extruded copolymer turns from clear
32 to cloudy, and when a strand of the cooled copolymer is

1 pulled in the direction in which it was extruded, the cloudy
2 copolymer turns whitish and opaque.

3 (c) % saponified

4 The extent of saponification is defined as the percent of
5 moles of esters of alpha, beta-ethylenically-unsaturated
6 carboxylic acids converted to metal salts of acrylic and
7 methacrylic acid. Compositions of this invention have been
8 produced where the extent of saponification of the ester
9 groups in the copolymer has been between about 25 and 99%.
10 Ionomer which has an extent of saponification below about
11 25% above are typically cloudy and have poorer gloss, melt
12 strength, and/or tensile strength than compositions of this
13 invention. A greater extent of saponification generally
14 produces low-haze ionomers more consistently than a low
15 extent of saponification, particularly when the reaction
16 temperature is between about 150 and 225°C.

17 C. Acidification

18 Acidification of a polymer is a useful method for modifying
19 polymer properties. In one preferred embodiment, ionomers
20 of this invention have essentially no acidity. These
21 ionomers can be represented as copolymers comprising
22 comonomers of alpha-olefins, esters of alpha, beta-
23 ethylenically-unsaturated carboxylic acids, and metal salts
24 of alpha, beta-ethylenically-unsaturated carboxylic acids.
25 The properties of these non-acidic ionomers can be modified
26 by adding acid groups.

27 Also, some of the ionomers of this invention are highly
28 water-dispersible. This can be an advantage for
29 applications where repulpable compositions are desired, such
30 as repulpable paper coatings and adhesives. However, water
31 dispersibility is a problem where the ionomer composition is
32 cooled in a water-bath after saponification, which is a

1 common commercial method of cooling polymers. Much of the
2 ionomer to be cooled can end up dispersed in the cooling
3 water, turning the water a milky white color.

4 Other cooling means may be used for handling highly water-
5 dispersible ionomers, such as hot-face cutting or utilizing
6 an air-cooled conveyor or a conveyor which has a water-
7 chilled surface to cool the polymer strands or pellets.
8 However, these methods are more expensive and less efficient
9 than passing hot polymer in the form of strands, pellets, or
10 film through a water bath, and these methods require the
11 installation of new equipment in many existing commercial
12 ionomer production facilities. In addition, ionomer may
13 discolor when using these cooling means, since the ionomer
14 rapidly oxidizes when it is maintained at elevated
15 temperatures for the extended periods of time inherent in
16 these other cooling means.

17 (1) Cooling ionomer in an aqueous acid bath

18 In a preferred embodiment, highly water-dispersible ionomer
19 of this invention may be cooled in an acid bath to prevent
20 dispersion of much of the ionomer. Highly water-dispersible
21 ionomer typically has a high sodium acrylate content which
22 makes the ionomer water-soluble. It is believed that ion
23 exchange occurs predominantly on the surface of the polymer
24 when passing hot ionomer strands through the acid bath,
25 replacing metal ions on the surface of the polymer with
26 hydrogen ions from the acid. It is believed that this makes
27 the surface of the strands or pellets acidic and
28 substantially reduces their water solubility.

29 Infrared analysis of ionomer pellets which were cooled in an
30 acid bath detected no acid groups. However, it is believed
31 that the concentration of acid groups in the overall ionomer

1 pellets was so small that it was undetectable by infrared
2 analysis of the bulk ionomer.

3 Almost any inorganic or water-soluble organic acid can be
4 used in the acid bath. A dilute aqueous solution of a non-
5 oxidizing acid is preferred to reduce processing cost and to
6 improve the washing efficiency when rinsing any excess acid
7 off of the polymer. The following list is illustrative of
8 the types of acids which may be used: sulfuric acid, formic
9 acid, propionic acid, oxalic acid, and the like. Preferred
10 acids are hydrochloric acid, phosphoric acid, and acetic
11 acid.

12 The temperature of the acid solution is preferably that
13 temperature which produces ionomer which has not discolored
14 and which provides ionomer at the appropriate temperature
15 for any subsequent processing steps, such as drying. The
16 temperature of the acid solution is typically between about
17 5 to 50°C, and preferably is between about 10 and 30°C.

18 Example 16 illustrates this method for cooling ionomer using
19 an aqueous acid solution.

20 (2) Acidification of a clear copolymer of
21 ethylene and esters and metal salts of alpha.
22 beta-ethylenically-unsaturated carboxylic
23 acids

24 In one embodiment, compositions of this invention have
25 carboxylic acid groups, in which case the compositions can
26 be represented as copolymers comprising comonomers of alpha-
27 olefins, esters of alpha, beta-ethylenically-unsaturated
28 carboxylic acids, metal salts of alpha, beta-ethylenically-
29 unsaturated carboxylic acids, and alpha, beta-ethylenically-
30 unsaturated carboxylic acids. Acid groups can plasticize
31 the composition and increase its melt index. This permits

1 tailoring of polymer properties such as polymer flow
2 viscosity, tear strength, polymer reactivity with food, and
3 odor or taste for a particular application.

4 Acidification of a composition comprising a copolymer of
5 alpha-olefins, esters of alpha, beta-ethylenically-
6 unsaturated carboxylic acids, and metal salts of alpha,
7 beta-ethylenically-unsaturated carboxylic acids can occur in
8 a reaction section of a reactive extruder. Preferably,
9 acidification occurs in a second reaction section when using
10 reactive extrusion, and preferably after the composition
11 comprising the reaction product of a copolymer of alpha-
12 olefins and esters of alpha, beta-ethylenically-unsaturated
13 carboxylic acids has been saponified with a Group IA metal-
14 containing solution in a first reaction section.

15 Other equipment may be used in place of a reactive extruder
16 for acidification of a saponified composition. For example,
17 a Brabender Plasticorder, a resin kettle, or an autoclave
18 may be used.

19 A non-oxidizing acid can be used at a temperature and in a
20 concentration which does not cause significant degradation
21 of the copolymer or composition. Typically, the amount of
22 acid required is the amount which provides the desired
23 weight percent of acid groups per combined weight of acid
24 and copolymer to be acidified. Examples of these acids
25 include phosphoric acid, hydrochloric acid, benzoic acid,
26 lactic acid, and stearic acid. Polymeric non-oxidizing
27 acids can also be used, such as ethylene-acrylic acid
28 copolymer, exemplified by Dow Chemical Company's Primacor
29 Grade 3330. The non-oxidizing acids may have only one or
30 two monomer units, such as benzoic acid or acetic acid, or
31 they may comprise polymeric acids having multiple monomer
32 units and having a molecular weight well in excess of one

1 million, such as Primacor Grade 3330. Phosphoric acid,
2 lactic acid, and polymer acids are preferred. Typical
3 temperatures for acidification are between about 190 and
4 300°C, and preferably are between about 230 and 300°C. The
5 acid concentration is preferably between 10 and 95%.

6 In certain applications or compositions of this invention,
7 any byproducts of acidification can remain in the
8 composition. For other applications or compositions, any
9 byproducts of acidification and/or any excess acid can be
10 removed from the ionomer by washing with water or other
11 solvent and filtering the composition. For example, polymer
12 acidified using phosphoric acid can be washed with water in
13 an autoclave. The byproduct salt in the aqueous phase can
14 subsequently be separated from the polymer by filtration.

15 D. Uses of the compositions

16 Ionomer compositions of this invention can be formed into
17 single or multi-layer films using conventional equipment.
18 For example, cast, extruded, or blown film can be made.

19 An ionomer composition of this invention can be coextruded
20 with or laminated to other polymers such as nylon
21 (unoriented and oriented), polyester (unoriented and
22 oriented), polystyrene, polyvinyl acetate,
23 polyacrylonitrile, polyvinylidene dichloride, and
24 polyolefins such as polypropylene (unoriented and oriented),
25 polyethylene (low density, high density, and linear low
26 density), ethylene-methyl (meth)acrylate copolymers,
27 ethylene-ethyl (meth)acrylate copolymers, ethylene-
28 (meth)acrylic acid copolymers, ethylene-vinyl alcohol
29 copolymers, ethylene vinyl acetate copolymers, and other
30 polymers and their derivatives capable of being coextruded.
31 Typical uses for ionomer compositions of this invention
32 include their use in single-layer or multi-layer films,

1 where they can be used as tie layers or used for imparting
2 flexibility, toughness, strength, hot tack, and/or heat seal
3 capabilities. Such uses include stretch films, bundling
4 (shrink) wrap, food and drug packaging, and skin packaging
5 for protecting the contents of a package. A layer of
6 ionomer of this invention can withstand higher temperatures
7 encountered in some end-uses, such as cook-in bags or
8 autoclave sterilization. Also, the ionomer of this
9 invention has high adhesion to other organic materials such
10 as other polymers or even natural polymers such as the
11 protein found in meat and cheese.

12 Single-layer ionomer film or multi-layer film in which the
13 ionomer is on one face of the film can be used as a surface
14 protection layer for products such as glass, polycarbonate
15 or poly(methyl methacrylate) products, which can be used in
16 windshields for vehicles or windows. The ionomer layer
17 protects products from scratches and/or nicks because of the
18 ionomer's abrasion resistance. The ionomer's adhesion to
19 such substrates is excellent, yet it can be peeled readily
20 from the surface. The transparency of the ionomer of this
21 invention allows visual inspection of the surface of the
22 wrapped product, permitting a customer to inspect a product
23 for flaws prior to receipt and unwrapping of the product.

24 Ionomer of this invention can also be used as a glass inter-
25 layer. The ionomer provides shatter resistance, sound
26 dampening, and/or bullet-proof characteristics to the glass
27 structure incorporating the ionomer.

28 Single-layer ionomer film or multi-layer film containing
29 ionomer of this invention can be used to make easy-open
30 packaging such as easy-tear film, bags, pouches and parcels.
31 A tear propagates linearly through the film, both in the
32 machine and transverse directions in blown and cast films,

1 and the Elmendorf tear strength of the ionomer indicates
2 that it is well-suited to uses such as easy-opening
3 packaging. The package in which the film is incorporated
4 normally is notched or incorporates a tear strip to
5 facilitate ease of opening of the package.

6 The ionomer of this invention can also serve as its own tie
7 layer due to its good adhesion to other layers. This
8 eliminates the need for separate tie layers in a multi-layer
9 film, reducing the thickness of the multi-layer film and
10 reducing the overall cost of making the multi-layer film.

11 Ionomer of this invention can be blended with other polymers
12 to modify the properties of the ionomer and/or the polymer
13 with which it is blended. Ionomer of this invention forms
14 compatible blends with many polymers. The ionomer can
15 improve processability of polymers such as ethylene-vinyl
16 alcohol copolymer and polyesters. Ionomer can be used to
17 adjust many properties of the blended composition, such as
18 the elasticity, impact resistance, amount of shrinkage of
19 polymer used in injection-molding, softness, flexibility,
20 heat seal, hot tack, and brittleness, and can be used in
21 those applications where ionomer alone is used.

22 The ionomer of this invention can also be used alone or in
23 combination with other polymers to make peelable seals.

24 Polymers with which the ionomer of this invention may be
25 blended include ethylene-acrylic acid and -methacrylic acid
26 copolymers; other ionomers such as ethylene-acrylic acid and
27 -methacrylic acid ionomers partially neutralized with
28 sodium, zinc, lithium, and/or other cations; ethylene alkyl
29 acrylate and methacrylate copolymers, including ethylene-
30 methyl acrylate copolymer, ethylene-methyl methacrylate
31 copolymer, ethylene-ethyl acrylate copolymer and ethylene-

1 butyl acrylate copolymer; ethylene-vinyl acetate copolymer;
2 polyolefins, including low, linear low, medium and high-
3 density polyethylene, polypropylene, and polybutadiene;
4 ethylene vinyl alcohol copolymer; polyamides, including
5 nylon 6, nylon 12 and nylon 6,6; polyesters, including
6 poly(ethylene terephthalate); polycarbonates; polystyrene,
7 including high-impact polystyrene, acrylonitrile-butadiene-
8 styrene copolymer, and block copolymers of styrene and
9 butadiene; poly(vinyl chloride); polyurethane; and epoxy
10 resins.

11 Ionomer of this invention blends well with ethylene alkyl
12 acrylate and/or methacrylate copolymers. The ionomer and
13 copolymer form compatible blends, where there is little or
14 no phase separation. Blending permits tailoring the heat
15 seal and hot tack properties for particular uses.

16 Ionomer of this invention may also be cross-linked to other
17 polymers that have reactive groups. Cross-linking can be
18 achieved by irradiation, by organic peroxide-induced cross-
19 linking, or via acidolysis or transesterification. In this
20 manner, properties such as melt-point temperature,
21 processability, elasticity, impact resistance, amount of
22 shrinkage of polymer used in injection-molding, softness,
23 flexibility, heat seal, hot tack, and brittleness may be
24 further modified. A polymer having a reactive group is one
25 typically formed by reacting bi- or tri- or multi-functional
26 monomers to form polymers having at least one functional
27 (i.e. reactive) group on the side and/or end of the polymer
28 backbone. The reactive group is one that is capable of
29 participating in an acidolysis or a transesterification
30 reaction.

31 Examples of polymers with which ionomer of this invention
32 may be cross-linked through reactive groups via acidolysis

1 include polyesters, such as poly(ethylene terephthalate),
2 polyamides, such as nylon 6 and nylon 6,6, polyurethanes,
3 and polycarbonates. In these polymers, the functional or
4 reactive group is an amine or a carboxyl group. Examples of
5 polymers with which ionomer of this invention may be cross-
6 linked through a reactive group via transesterification
7 include polyesters and ethylene-alkyl acrylate and
8 -methacrylate copolymers. In these polymers, the functional
9 or reactive group is a carboxyl group or an ester.

10 Cross-linking may occur in any equipment suitable to acidify
11 or transesterify the polymers. A twin-screw reactive
12 extruder can be used to form a melt blend of the ionomer and
13 polymer with which the ionomer will be linked and to perform
14 the acidification or transesterification. The acid or
15 transesterification catalyst may be fed to the extruder with
16 the ionomer and polymer to which the ionomer is to be
17 linked, and/or the acid or transesterification catalyst may
18 be fed directly to a reaction zone of the reactive extruder.
19 Many acids may be used in the acidification reaction, but
20 preferably the acid is a weak organic acid such as carbonic
21 or acetic acid. Any transesterification catalyst may be
22 used, but preferably the catalyst is a titanate such as
23 tetraethyl titanate. A reactive extruder typically has a
24 devolatilization section to remove volatile byproducts of
25 acidification or transesterification, and if desired, the
26 reacted blend may also be treated with a high pH compound
27 such as sodium hydroxide or soda ash to remove any excess
28 acidity after acidification. The properties of a blend of
29 ionomer and other polymers can thus be further modified by
30 cross-linking the blend.

31 Ionomer compositions of this invention may also be used in
32 thermally extruded and thermally formed products such as
33 automotive interior parts and skin packaging. The ionomer

1 compositions may be used alone or in combination with other
2 polymers in blow-molded or injection molded articles,
3 particularly where such articles need to be grease- and oil-
4 resistant such as bottles for fragrances or detergents, and
5 the compositions may also be used in articles such as food
6 trays formed by vacuum thermo-forming. The ionomer
7 compositions of this invention may be used in making
8 articles such as golf ball covers; coated fabrics;
9 orthopedic, prosthetic and medical devices; recreational
10 equipment; and footwear components. The ionomer
11 compositions of this invention are especially useful in
12 applications where the ionomer properties discussed above,
13 as well as the excellent abrasion resistance, transparency,
14 and/or directional tear properties of the ionomer, are
15 useful.

16 Theories discussed herein are intended to provide possible
17 explanations for what was observed. These theories are not
18 to be interpreted as limiting the invention described
19 herein. Also, the following examples are illustrative and
20 are not intended to limit the invention disclosed herein.

21 EXAMPLE 1

22 An ethylene-methyl acrylate copolymer (manufactured by
23 Chevron by the method disclosed in U.S. Patent
24 No. 3,350,372) containing 20% by weight methyl acrylate
25 (7.5 mole %) and having a melt index of 400 g/10 min.
26 (190°C) was fed to a Werner & Pfleiderer corrosion-resistant
27 ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. The
28 extruder had a ratio of length to diameter of about 44. The
29 screw configuration for Examples 1-13 and Comparative
30 Example A is given in Table 1 column A. Aqueous sodium
31 hydroxide (50% NaOH by weight in all examples, except where
32 noted otherwise) was fed to Zone 3 of the extruder at
33 9.3 lbs./hr. The screw speed was 550 rpm.

1 The following extruder temperatures were measured:

2 Table 2

3 Zone No.	1	2	3	4	5	6	7
4 Temperature 5 (°C)	236	350	253	253	230	245	260

6 Note: Zone 1: melting section for polymer to be reacted;
7 Zone 2 & 3: reaction section;
8 Zone 4: devolatilization section;
9 Zones 5-7: extrusion section.

10 Water from the sodium hydroxide solution and the reaction
11 by-product methanol were removed by a two-stage
12 devolatilization. In all examples, the evolved water and
13 methanol from the first devolatilization stage were
14 condensed at atmospheric pressure. The second
15 devolatilization stage was connected to a vacuum system in
16 all examples. The second devolatilization stage had 28.4
17 in. Hg vacuum during this run.

18 The reaction product was extruded through an eight-strand
19 die, cooled on a stainless steel belt (about 20 feet in
20 length, made by Sandvik) which was chilled by cold water
21 underneath the belt, and subsequently pelletized.

22 The product had a melt flow rate of 0.33 g/10 min. (230°C).
23 The product had a hydrolysis of 53% (i.e., 53% of the methyl
24 acrylate in the ethylene-methyl acrylate copolymer was
25 converted to sodium acrylate).

26 The polymer was made into blown film on a Victor blown film
27 line at the following processing conditions:

Table 3

Zone 1	Zone 2	Zone 3	Adapter	Die 1	Die 2	Die Pressure	Melt Temperature
400°F	440°F	515°F	435°F	430°F	440°F	7600 psi	440°F

The blown film had a thickness of 3.5 mils. The haze of the film was 2%, and the 60° gloss was 122. The 1% secant moduli of the film were 12,740 and 10,080 psi respectively for the machine direction (MD) and the transverse direction (TD).

All haze values were measured using the method of ASTM D 1003. The 60° gloss values were measured using the method of ASTM D 2457. The 1% secant modulus values and tensile strength values were measured using the method of ASTM D-638.

Melt index of feed resin was measured by the method of ASTM D 1239, using a temperature of 190°C and a 2.16 kg weight. The melt flow rate of a composition of this invention was determined by the method of ASTM D 1239 but using a temperature of 230°C rather than 190°C and using a 2.16 kg weight.

The hydrolysis of the product is defined as the moles of metal salt of the alpha, beta-ethylenically-unsaturated carboxylic acid present in the product, expressed as a percentage of the moles of the ester of alpha, beta-ethylenically-unsaturated carboxylic acid present prior to saponifying the copolymer. The terms "hydrolysis", "extent of hydrolysis", "percent hydrolysis", "percent saponified", and "extent of saponification" are used interchangeably.

1 The extent of hydrolysis is determined by dissolving 10 g.
2 of ionomer in 250 ml. of tetrahydrofuran (THF) in a 500 ml.
3 round-bottom flask, to which 1 ml. of glacial acetic acid is
4 added. The flask is fitted with a refluxing condenser, and
5 the contents are boiled for about 20 min. The mixture is
6 poured into 1 liter of cold distilled water (about 15-20°C),
7 and then filtered. The precipitate is subsequently washed
8 with about 3 liters of distilled water. The precipitate is
9 dried under vacuum, then weighed and dissolved in THF and
10 titrated with 0.1 N potassium hydroxide in ethanol, using
11 thymol blue to indicate the end-point of titration. The
12 extent of hydrolysis is then calculated by dividing the
13 moles of potassium used in titrating the sample by the moles
14 of ester present in the initial ethylene-methyl acrylate
15 copolymer prior to the saponification reaction.

16 EXAMPLE 2

17 The ethylene-methyl acrylate copolymer of Example 1 was fed
18 to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin
19 screw extruder at a rate of 100 lbs./hr. Aqueous sodium
20 hydroxide was fed to Zone 3 of the extruder at a rate of
21 11.2 lbs./hr. The screw speed was 500 rpm.

22 The following temperatures were measured during the process:

23 Table 4

24 Zone No.	1	2	3	4	5	6	7
25 Temperature	271	252	255	256	230	231	241
26 (°C)							

27 The vacuum on the second devolatilization zone was 28.4 in.
28 Hg. The reaction product was extruded, cooled on a Sandvik
29 belt and pelletized in the same way as Example 1. The
30 product had a melt flow rate of 0.20 g/10 min. (230°C). The
31 hydrolysis of the product was 65%.

1 The polymer was made into blown film on a Victor blown film
2 line using the processing conditions similar to those in
3 Example 1. The haze of the blown film was 2%, and the 60°
4 gloss was 133. The film had a tensile strength of 4010 and
5 3180 psi respectively for MD and TD. The 1% secant moduli
6 of the film were 14720 and 13110 psi respectively for MD and
7 TD.

8 EXAMPLE 3

9 The ethylene-methyl acrylate copolymer of Example 1 was fed
10 to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin
11 screw extruder at a rate of 100 lbs./hr. Aqueous sodium
12 hydroxide was fed to Zone 3 on the extruder at a rate of
13 12.1 lbs./hr. The screw speed was 500 rpm.

14 The following temperatures were measured during the process:

15 Table 5

16 Zone No.	1	2	3	4	5	6	7
17 Temperature 18 (°C)	218	347	255	255	230	251	260

19 The vacuum on the second devolatilization zone was 28.5 in.
20 Hg. The reaction product was extruded, cooled on a Sandvik
21 belt and pelletized in the same way as Example 1. The
22 product had a melt flow rate of 0.1 g/10 min. (230°C). The
23 hydrolysis of the product was 70%.

24 The polymer was made into blown film on a Victor blown film
25 line using the processing conditions similar to those in
26 Example 1. The haze of the blown film was 2%, and the 60°
27 gloss was 134. The film had a tensile strength of 4470 and
28 2420 psi respectively for MD and TD.

EXAMPLE 4

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 570 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3 on the extruder at a rate of 13.0 lbs./hr. The screw speed was 500 rpm.

The following temperatures were measured during the process:

Table 6

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	178	242	254	252	301	303	289

The vacuum on the second devolatilization zone was 25.5 in. Hg. The reaction product was extruded, cooled on a Sandvik belt and pelletized in the same way as Example 1. The product had a melt flow rate of 0.87 g/10 min. (230°C). The hydrolysis of the product was 69%.

The polymer was made into blown film on a Victor blown film line using the processing conditions similar to those in Example 1. The haze of the blown film was 2%, and the 60° gloss (ASTM D 2457) was 135. The film had a tensile strength of 2870 and 1760 psi respectively for MD and TD.

EXAMPLE 5

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 440 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3

1 on the extruder at a rate of 13.0 lbs./hr. The screw speed
2 was 500 rpm.

3 The following temperatures were measured during the process:

4 Table 7

5 Zone No.	1	2	3	4	5	6	7
6 Temperature 7 (°C)	189	257	257	258	251	263	283

8 The vacuum on the second devolatilization zone was 28.4 in.
9 Hg. The reaction product was extruded, cooled on a Sandvik
10 belt and pelletized in the same way as Example 1. The
11 product had a melt flow rate of 0.81 g/10 min. (230°C). The
12 hydrolysis of the product was 72%.

13 The polymer was made into blown film on a Victor blown film
14 line using the processing conditions similar to those in
15 Example 1. The haze of the blown film was 2%, and the 60°
16 gloss was 135. The film had a tensile strength of 2600 and
17 1850 psi respectively for MD and TD.

18 EXAMPLE 6

19 An ethylene-methyl acrylate copolymer containing 23% by
20 weight methyl acrylate and having a melt index of
21 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer
22 corrosion-resistant ZSK-40mm twin screw extruder at a rate
23 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3
24 on the extruder at a rate of 10.7 lbs./hr. The screw speed
25 was 500 rpm.

1 The following temperatures were measured during the process:

Table 8

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	181	247	256	255	255	254	270

6 The vacuum on the second devolatilization zone was 26.7 in.
7 Hg. The reaction product was extruded, cooled on a Sandvik
8 belt and pelletized in the same way as Example 1. The
9 product had a melt flow rate of 0.54 g/10 min. (230°C). The
10 hydrolysis of the product was 51%.

11 The polymer was made into blown film on a Victor blown film
12 line using the processing conditions similar to those in
13 Example 1. The haze of the blown film was 2%, and the 60°
14 gloss was 124. The film had a tensile strength of 2270 and
15 1470 psi respectively for MD and TD.

EXAMPLE 7

16 An ethylene-methyl acrylate copolymer containing 23% by
17 weight methyl acrylate and having a melt index of
18 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer
19 corrosion-resistant ZSK-40mm twin screw extruder at a rate
20 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3
21 on the extruder at a rate of 12.8 lbs./hr. The screw speed
22 was 500 rpm.
23

24 The following temperatures were measured during the process:

Table 9

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	175	247	253	259	254	257	271

1 The vacuum on the second devolatilization zone was 26.6 in.
2 Hg. The reaction product was extruded, cooled on a Sandvik
3 belt and pelletized in the same way as Example 1. The
4 product had a melt flow rate of 0.45 g/10 min. (230°C). The
5 hydrolysis of the product was 61%.

6 The polymer was made into blown film on a Victor blown film
7 line using the processing conditions similar to those in
8 Example 1. The haze of the blown film was 3%, and the 60°
9 gloss was 132. The film had a tensile strength of 2730 and
10 1960 psi respectively for MD and TD.

11 **EXAMPLE 8**

12 An ethylene-methyl acrylate copolymer containing 23% by
13 weight methyl acrylate and having a melt index of
14 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer
15 corrosion-resistant ZSK-40mm twin screw extruder at a rate
16 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3
17 on the extruder at a rate of 9.6 lbs./hr. The screw speed
18 was 500 rpm.

19 The following temperatures were measured during the process:

20 Table 10

21 Zone No.	1	2	3	4	5	6	7
22 Temperature 23 (°C)	193	284	257	259	254	254	271

24 The vacuum on the second devolatilization zone was 26.2 in.
25 Hg. The reaction product was extruded, cooled on a Sandvik
26 belt and pelletized in the same way as Example 1. The
27 product had a melt flow rate of 0.60 g/10 min. (230°C). The
28 hydrolysis of the product was 46%.

1 The polymer was made into blown film on a Victor blown film
2 line using the processing conditions similar to those in
3 Example 1. The haze of the blown film was 2%, and the 60°
4 gloss was 120. The film had a tensile strength of 1950 and
5 1240 psi respectively for MD and TD.

6 EXAMPLE 9

7 An ethylene-methyl acrylate copolymer containing 22% by
8 weight methyl acrylate and having a melt index of
9 470 g/10 min. (190°C) was fed to the Werner & Pfleiderer
10 corrosion-resistant ZSK-40mm twin screw extruder at a rate
11 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3
12 on the extruder at a rate of 14.3 lbs./hr. The screw speed
13 was 500 rpm.

14 The following temperatures were measured during the process:

15 Table 11

16 Zone No.	1	2	3	4	5	6	7
17 Temperature 18 (°C)	298	326	255	266	254	254	271

19 The vacuum on the second devolatilization zone was 28.4 in.
20 Hg. The reaction product was extruded, cooled on a Sandvik
21 belt and pelletized in the same way as Example 1. The
22 product had a melt flow rate of 0.23 g/10 min. (230°C). The
23 hydrolysis of the product was 70%.

24 The polymer was made into blown film on a Victor blown film
25 line using the processing conditions similar to those in
26 Example 1. The haze of the blown film was 1%, and the 60°
27 gloss was 134. The film had a tensile strength of 3000 and
28 2170 psi respectively for MD and TD.

EXAMPLE 10

An ethylene-methyl acrylate copolymer containing 23% by weight methyl acrylate and having a melt index of 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3 on the extruder at a rate of 8.6 lbs./hr. The screw speed was 500 rpm.

The following temperatures were measured during the process:

Table 12

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	177	262	255	253	254	255	270

The vacuum on the second devolatilization zone was 25.8 in. Hg. The reaction product was extruded, cooled on a Sandvik belt and pelletized in the same way as Example 1. The product had a melt flow rate of 1.25 g/10 min. (230°C). The hydrolysis of the product was 41%.

The polymer was made into blown film on a Victor blown film line using the processing conditions similar to those in Example 1. The haze of the blown film was 4%, and the 60° gloss was 104. The film had a tensile strength of 1910 and 970 psi respectively for MD and TD.

EXAMPLE 11

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 100 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3

1 on the extruder at a rate of 4.7 lbs./hr. The screw speed
2 was 500 rpm.

3 The following temperatures were measured during the process:

Table 13

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	253	322	254	230	230	231	241

8 The vacuum on the second devolatilization zone was 28.4 in.
9 Hg. The reaction product was extruded, cooled on a Sandvik
10 belt and pelletized in the same way as Example 1. The
11 product had a melt flow rate of 0.67 g/10 min. (230°C). The
12 hydrolysis of the product was 26%.

13 The polymer was made into blown film on a Victor blown film
14 line using the processing conditions similar to those in
15 Example 1. The haze of the blown film was 3%, and the 60°
16 gloss was 115. The film had a tensile strength of 1150 and
17 1080 psi respectively for MD and TD.

EXAMPLE 12

18 An ethylene-methyl acrylate copolymer containing 20% by
19 weight methyl acrylate and having a melt index of
20 400 g/10 min. (190°C) was fed to the Werner & Pfleiderer
21 corrosion-resistant ZSK-40mm twin screw extruder at a rate
22 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3
23 on the extruder at a rate of 9.3 lbs./hr. The screw speed
24 was 500 rpm.
25

1 The following temperatures were measured during the process:

2 Table 14

3 Zone No.	1	2	3	4	5	6	7
4 Temperature 5 (°C)	209	201	266	255	256	256	256

6 The vacuum on the second devolatilization zone was 24.7 in.
7 Hg. The reaction product was extruded, cooled in a water
8 bath, and pelletized. The pellets were dried in a vacuum
9 over at 65°C and 29.5 in. Hg for 48 hours. The product had
10 a melt flow rate of 0.66 g/10 min. (230°C). The hydrolysis
11 of the product was 49%.

12 The polymer was made into blown film on a Victor blown film
13 line using the processing conditions similar to those in
14 Example 1. The haze of the blown film was 3%, and the 60°
15 gloss was 128.

16 EXAMPLE 13

17 An ethylene-methyl acrylate copolymer containing 20% by
18 weight methyl acrylate and having a melt index of
19 150 g/10 min. (190°C) was fed to the Werner & Pfleiderer
20 corrosion-resistant ZSK-40mm twin screw extruder at a rate
21 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3
22 on the extruder at a rate of 7.4 lbs./hr. The screw speed
23 was 450 rpm.

24 The following temperatures were measured during the process:

25 Table 15

26 Zone No.	1	2	3	4	5	6	7
27 Temperature 28 (°C)	188	199	276	253	257	260	262

1 The vacuum on the second devolatilization zone was 28.5 in.
2 Hg. The reaction product was extruded, cooled in a water
3 bath, and pelletized. The pellets were dried in a vacuum
4 over at 65°C and 29.5 in. Hg for 48 hours. The product had
5 a melt flow rate of 0.22 g/10 min. (230°C). The hydrolysis
6 of the product was 42%.

7 The polymer was made into blown film on a Victor blown film
8 line using the processing conditions similar to those in
9 Example 1. The haze of the blown film was 4%, and the 60°
10 gloss was 122.

11 EXAMPLE 14

12 An ethylene-methyl acrylate copolymer containing 20% by
13 weight methyl acrylate and having a melt index of
14 400 g/10 min. (190°C) was fed to a Werner & Pfleiderer
15 ZSK-58mm twin screw extruder at a rate of 425 lbs./hr. The
16 screw was configured to provide substantially the same
17 mixing as provided in the ZSK-40mm extruder in Examples 1-
18 13. Aqueous sodium hydroxide was fed to the reaction zone
19 on the extruder at a rate of 56 lbs./hr.

20 The screw speed of the extruder was at 500 rpm. The
21 temperatures in the reaction zones were 226°C to 338°C. The
22 product was 71% hydrolyzed. The product had similar optical
23 properties to the product of Example 3.

24 EXAMPLE 15

25 An ethylene-methyl acrylate copolymer containing 20% by
26 weight methyl acrylate and having a melt index of
27 400 g/10 min. (190°C) was fed to a Werner & Pfleiderer
28 ZSK-70mm twin screw extruder at a rate of 450 lbs./hr. The
29 screw was configured to provide substantially the same
30 mixing as provided in the ZSK-40mm extruder in Examples 1-

13. Aqueous sodium hydroxide was fed to the reaction zone on the extruder at a rate of 50 lbs./hr.

The screw speed of the extruder was at 580 rpm. The temperatures in the reaction zones were 330°C to 350°C. The product was 61% hydrolyzed. The product had similar optical properties to the product of Example 3.

COMPARATIVE EXAMPLE A

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 20 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3 on the extruder at a rate of 4.6 lbs./hr. The screw speed was 400 rpm.

The following temperatures were measured during the process:

Table 16

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	216	213	270	269	270	271	270

The vacuum on the second devolatilization zone was 27.9 in. Hg. The reaction product was extruded, cooled in a water bath, and pelletized. The pellets were dried in a vacuum oven at 65°C and 29.5 in. Hg for 48 hours. The product had a melt flow rate of 3.2 g/10 min. (190°C). The hydrolysis of the product was 15%.

The polymer was made into blown film on a Victor blown film line using the processing conditions similar to those in Example 1. The haze of the blown film was 81%, and the 60° gloss was 35.

1 This Comparative Example A shows that saponifying 15% of the
2 methyl acrylate groups to form the sodium salt of acrylic
3 acid is insufficient at these reaction conditions to produce
4 the low haze of compositions of this invention.

5 COMPARATIVE EXAMPLE B

6 An ethylene-methyl acrylate copolymer containing 20% methyl
7 acrylate by weight and having a melt index of 400 g/10 min.
8 was fed to a Werner & Pfleiderer ZSK-30 corrosion-resistant
9 extruder at 13.2 lbs/hr. 1.73 lbs/hr. of 35% sodium
10 hydroxide solution was fed to zone 3 of the extruder. The
11 extruder had the configuration of elements shown in Table 1
12 column B.

13 The following extruder temperatures were measured:

14 Table 17

15 Zone No.	1	2	3	4	5	6	7
16 Temperature 17 (°C)	230	275	275	275	275	240	235

18 Water and the by-product methanol were removed in a two-
19 stage devolatilization zone. The polymer strands were
20 cooled in a water bath and pelletized. The pellets were
21 vacuum-dried overnight at about 25 in. Hg vacuum and at
22 68°C.

23 Chemical analysis of the product indicated a degree of
24 saponification of 49.2%. The product had a melt index
25 (190°C) of 0.54 g/10 min.

26 A 1/2 inch Randcastle miniextruder was used to make a cast
27 film of about 4 inch width. The temperature at the feed
28 zone and barrels 1A through 3A was 430°C, while the die

1 temperature was 440°C. The film had a haze of 55% and a 60°
2 gloss of 20.

3 It is believed that the poor clarity of this example results
4 from a more dilute caustic solution and poorer mixing at
5 these reaction conditions as compared to the conditions
6 which produce compositions of this invention.

7 COMPARATIVE EXAMPLE C

8 An ethylene-methyl acrylate copolymer containing 20% methyl
9 acrylate by weight and having a melt index of 400 g/10 min.
10 was fed to a Werner & Pfleiderer ZSK-30 corrosion-resistant
11 extruder at 13.2 lbs/hr. 2.29 lbs/hr. of 35% sodium
12 hydroxide solution was fed to zone 3 of the extruder. The
13 extruder had the configuration of elements shown in Table 1
14 column B.

15 The following extruder temperatures were measured:

16 Table 18

17 Zone No.	1	2	3	4	5	6	7
18 Temperature 19 (°C)	230	275	275	275	275	240	235

20 Water and the by-product methanol were removed in a two-
21 stage devolatilization zone. The polymer strands were
22 cooled in a water bath and pelletized. The pellets were
23 vacuum-dried overnight at about 25 in. Hg vacuum and at
24 68°C.

25 Chemical analysis of the product indicated a degree of
26 saponification of 65.2%. The product had a melt flow rate
27 of 0.38 g/10 min. (230°C).

1 A 1/2 inch Randcastle miniextruder was used to make a cast
2 film of about 4 inch width. The temperature at the feed
3 zone and barrels 1A through 3A was 430°C, while the die
4 temperature was 440°C. The film had a haze of 15% and a 60°
5 gloss of 66.

6 This comparative example shows that a greater extent of
7 hydrolysis provided clearer ionomer, but mixing conditions
8 as supplied by the screw design of Table 1 column B when
9 using 35% aqueous caustic did not appear to provide the
10 intensive mixing and reaction conditions necessary to obtain
11 a haze of 10% or less.

12 COMPARATIVE EXAMPLE D

13 Ethylene-methyl acrylate copolymer having 20 weight percent
14 methyl acrylate and a 400 melt index (190°C) was saponified
15 with a 35% by weight aqueous solution of sodium hydroxide
16 per the method of Comparative Example B. The product was
17 60% saponified and had a melt index (190°C) of 0.06. The
18 tensile strength in the machine direction was 1582 psi.

19 COMPARATIVE EXAMPLE E

20 Ethylene-methyl acrylate copolymer having 25 weight percent
21 methyl acrylate and a 457 melt index (190°C) was saponified
22 with a 35% by weight aqueous solution of sodium hydroxide
23 per the method of Comparative Example B. The product was
24 44% saponified and had a melt index (190°C) of 0.04. The
25 tensile strength in the machine direction was 985 psi.

26 EXAMPLE 16 -- ACID BATH COOLING OF IONOMER

27 26.4 lbs./hr. of the ethylene-methyl acrylate copolymer of
28 Example 1 were fed to a Werner & Pfleiderer corrosion
29 resistant ZSK-30 twin-screw extruder having the
30 configuration of elements given in Table 1 column C. 50%

1 aqueous sodium hydroxide was fed into zone 3 at 2.5 lb./hr.
2 The screw speed was 500 rpm.

3 The following extruder temperatures were measured:

Table 19

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	174	200	255	260	254	267	255

8 Volatile components were removed in a two port
9 devolatilization section, and the second port had a vacuum
10 of 28 in. Hg. The polymer strands from a four-strand die
11 were cooled in a 5% phosphoric acid bath which was 10 ft.
12 long, and were then rinsed in a 2 ft. water bath and
13 pelletized in a Conair pelletizer.

14 During 1.75 hours of operation, the ionomer was efficiently
15 cooled and pelletized, and the acid bath remained acidic and
16 clear with no evidence of dissolved polymer. Total carbon
17 analysis of the cooling water (determined by potentiometric
18 titration) at the end of operation showed less than 20 ppm
19 of dissolved carbon. By contrast, when the same polymer was
20 cooled in water, the water bath became turbid and milky-
21 white within a few minutes of operation.

22 The resulting pellets were colorless, shiny, and clear.

23 EXAMPLE 17

24 This example shows a copolymer of ethylene, methyl acrylate,
25 sodium acrylate, and acrylic acid. First, ethylene-methyl
26 acrylate copolymer having 20 weight percent methyl acrylate
27 and 153 melt index (190°C) was saponified in a Werner-
28 Pfleiderer ZSK-30 twin-screw reactive extruder using 50%
29 aqueous sodium hydroxide and substantially the same reaction

1 conditions as Example 16. The extent of saponification was
2 42%. The pelletized ionomer was clear and glossy and had a
3 melt flow rate (230°C) of 0.17 g/10 min.

4 The ionomer pellets were fed to the extruder at a rate of 12
5 kg/hr. 85.6% aqueous phosphoric acid was fed to Zone 3 of
6 the extruder at a rate of 0.14 kg/hr., and the product was
7 extruded, cooled in a water bath, and pelletized.

8 The product retained its clear and glossy optical
9 properties, and the melt flow rate increased to 1.0 g/10
10 min. (230°C). Film that was made on the Randcastle mini-
11 extruder had a tensile strength in the machine direction of
12 2418 psi.

13 EXAMPLE 18

14 Ethylene-methyl acrylate copolymer having 20 weight percent
15 methyl acrylate and 400 melt index (190°C) was saponified in
16 a ZSK-30 extruder having the configuration of elements given
17 in Table 1 column C with 50% aqueous sodium hydroxide at a
18 reaction temperature of about 148°C. The screw speed was
19 500 rpm. The copolymer was fed to the extruder at a rate of
20 12 kg/hr., and the product was about 54% saponified. The
21 product was visually clear.

22 COMPARATIVE EXAMPLE F

23 Ethylene-methyl acrylate copolymer having 20 weight percent
24 methyl acrylate and 400 melt index (190°C) was saponified
25 with 50% aqueous sodium hydroxide in a ZSK-30 extruder
26 having the configuration of screw elements given in Table 1
27 column B at a reaction temperature of about 149°C. The
28 screw speed was 500 rpm. The copolymer was fed to the
29 extruder at a rate of 16 kg/hr., and the product was about
30 52% saponified. The product was visually cloudy.

This example shows that insufficient mixing was supplied by the screw configuration of Table 1 column B at these reaction conditions.

EXAMPLE 19

26.4 lbs./hr. of the ethylene-methyl acrylate copolymer of Example 1 were fed to a Werner & Pfleiderer corrosion resistant ZSK-30 twin-screw extruder having the configuration of elements given in Table 1 column C. 50% aqueous potassium hydroxide was fed into zone 3 at the rate given in Table 20. The screw speed was 500 rpm.

The extruder temperatures were substantially the same as those given in Table 19. Volatile components were removed in a two port devolatilization section, and the second port had a vacuum of 28 in. Hg. The following table summarizes the feed rate of potassium hydroxide, the melt flow rate (230°C), and the extent of saponification of the methyl acrylate groups.

TABLE 20

Feed rate (lb./hr.) of 50% aqueous potassium hydroxide	Melt flow rate of ionomer of this Example	Extent of saponification
1.87	1.66	27
2.62	0.60	37
3.74	0.23	53
5.28	0.07	78

COMPARATIVE EXAMPLE G

An ethylene-methyl acrylate copolymer containing 20% methyl acrylate by weight and having a melt index of 20 g/10 min. (190°C) was fed to a Werner & Pfleiderer ZSK-40 corrosion-resistant extruder at 100 lbs/hr. 4.7 lbs/hr. of 50% sodium

1 hydroxide solution was fed to zone 3 of the extruder. The
2 screw speed was 275 rpm.

3 The following extruder temperatures were measured:

4 Table 21

5 Zone No.	1	2	3	4	5	6	7
6 Temperature 7 (°C)	200	208	279	280	278	280	281

8 The vacuum on the second devolatilization zone was 27.0 in.
9 Hg. The reaction product was extruded, cooled in a water
10 bath, and pelletized. The pellets were dried in a vacuum
11 oven at 65°C and 29.5 in. Hg for 48 hours. The product had
12 a melt index of 1.6 g/10 min. (190°C). The hydrolysis of
13 the product was 24%.

14 The polymer was made into blown film on a Victor blown film
15 line using the processing conditions similar to those in
16 Example 1. The haze of the blown film was 97%, and the 60°
17 gloss was 43.

18 The SEM micrograph shown in Figure 2 was taken on a freeze-
19 fractured surface of the blown film made from this ionomer.

20 COMPARATIVE EXAMPLE H

21 An ethylene-methyl acrylate copolymer having 20 weight
22 percent methyl acrylate and a melt index of 153 g/10 min.
23 (190°C) was 35% hydrolyzed by the method of Comparative
24 Example A. The melt index of this ionomer was 9.7 g/10 min.
25 (190°C), and the haze of a cast film was 98%, the 60° gloss
26 was 6, and the tear strength (g/mil) in the machine
27 direction was 33 and in the transverse direction was 41.

EXAMPLE 20

- 1
- 2 An ethylene-methyl acrylate copolymer having 20 weight
- 3 percent methyl acrylate was saponified substantially by the
- 4 method of Example 1. The percent hydrolysis and properties
- 5 of the polymer are listed in the following Table 22.

TABLE 22

% HYDRO- LYZED	% HAZE	60° GLOSS	TENSILE STRENGTH, psi		1° SECANT MODULUS, psi		MELT POINT TEMP. °C	ELMENDORF TEAR STRENGTH, g/mil		ELONGATION @ BREAK, %	
			MD	TD	MD	TD		MD	TD	MD	TD
35	13.3	55	1709	1445	7893	7667	77	12	14	350	376
42	1.4	126	2081	1928	14831	14054	76	17	24	420	434
50	0.5	140	2321	1984	8193	7718	73	26	22	365	405

Melt point temperature was measured using a differential scanning calorimeter and standard methods well-known in the art.
 Elmendorf tear strength was measured using ASTM D-1922.
 Elongation at break was measured using ASTM D-882.

1 The hot tack strength for these ionomers is summarized in
2 Figure 3.

3 EXAMPLE 21

4 Samples of ethylene methyl acrylate copolymer having the
5 methyl acrylate contents in following Table 23 were
6 saponified to various degrees of hydrolysis using
7 substantially the method of Example 1. In addition,
8 ethylene methyl acrylate copolymers made by the method of
9 U.S. Ser. No. 07/947,870, filed Sep. 21, 1992, where all of
10 the methyl acrylate was fed to a first reaction zone of a
11 multi-zone high-pressure polymerization reactor, were
12 saponified to various degrees of hydrolysis. Table 23
13 summarizes the melt point temperatures of these ionomers.

14 Table 23

15 16 17 WT. % METHYL ACRYLATE	ETHYLENE METHYL ACRYLATE COPOLYMER MADE BY METHOD OF U.S. 3,350,372		ETHYLENE METHYL ACRYLATE COPOLYMER MADE BY METHOD OF U.S. SER. NO. 07/947,870	
	% HYDROLYZED	MELT POINT TEMP., °C	% HYDROLYZED	MELT POINT TEMP., °C
18 12	62	90	60	97
19 12	86	83	83	99
20 12	--	--	83	98
21 12	100	87	99	93
22 20	--	--	35	92
23 20	47	87	42	91
24 20	51	86	50	91
25 20	61	83	65	92
26 20	72	64	--	--
27 24	42	64	--	--

EXAMPLE 22

1
2 Ionomer was made substantially by the method of Example 1.
3 This ionomer was cast coextruded individually with three
4 polymers on a Randcastle Mini-Extruder to form three 2-layer
5 films, where each layer was 2 mil thick. Adhesion strength
6 of the 2-layer films was analyzed using TAPPI Uniform Method
7 541, "Adhesion to Non-Porous Flexible Substrates", which is
8 incorporated by reference in its entirety herein.
9 Ionomer/propylene film (Fina 3275) had an adhesion of 770
10 g/inch; ionomer/high density polyethylene (Chevron HiD®
11 9650) could not be separated; and ionomer/nylon (Allied
12 Chemical's Capron 8350) had an adhesion of 80 g/inch.

13 The heat seal strength of the ionomer/polyethylene film
14 above is summarized in Figure 4.

EXAMPLE 23

15
16 Ethylene-methyl acrylate-butyl acrylate copolymer containing
17 10 weight percent methyl acrylate and 10 weight percent
18 butyl acrylate is about 50% hydrolyzed substantially by the
19 method of Example 1. This yields an ethylene-methyl
20 acrylate-butyl acrylate-sodium acrylate copolymer. It is
21 expected that the methyl acrylate reacts at a faster rate
22 than the butyl acrylate, so more methyl acrylate is
23 converted to the sodium salt than butyl acrylate. This
24 product is useful in applications where a higher melt-point
25 temperature is desired, such as films or bags which contact
26 hot food or liquids.

EXAMPLE 24

27
28 Ionomer #1, ionomer of this invention having an extent of
29 saponification of 50%, was formed by saponifying ethylene-
30 methyl acrylate copolymer having 20 wt.% methyl acrylate
31 with aqueous sodium hydroxide by substantially the method of
32 Example 1. Ionomer #2, ionomer of this invention having an

1 extent of saponification of about 83%, was formed by
2 saponifying ethylene-methyl acrylate copolymer having 12
3 wt.% methyl acrylate with aqueous sodium hydroxide by
4 substantially the method of Example 1.

5 These ionomers were melt-blended in an twin-screw extruder.
6 with polypropylene (PROFAX 6523 polypropylene) or with high-
7 density polyethylene (Chevron HiD 9607, 6 melt index) in the
8 weight ratios given in Tables 24-26 below. Mold shrinkage
9 was determined by forming a tensile bar of ionomer in a mold
10 and comparing the longitudinal length of the tensile bar to
11 the mold length after the tensile bar sat for several days.
12 Notched Izod was determined by ASTM D-256, and Vicat
13 softening point was determined by ASTM D-1525.

14 Table 24
15 PROPERTIES OF POLYPROPYLENE BLENDED WITH IONOMER #1

16 PARTS POLYPROPYLENE	0	25	75	100
17 PARTS OF IONOMER #1	100	75	25	0
18 MOLD SHRINKAGE, 19 mil/in.	6	8	20	approx. 24 ¹
20 VICAT SOFTENING 21 POINT, °C	60	71	150	160
22 NOTCHED IZOD, 23 ft-lb/in. at room 24 temperature	7	12	2	0

25 ¹ Value estimated from literature

26 This data shows surprisingly little mold shrinkage and
27 surprisingly improved impact resistance (as measured by
28 notched Izod) for a blend of ionomer of this invention and
29 polypropylene when less than about 50% of the blend is
30 polypropylene.

31 Table 25

1 PROPERTIES OF POLYPROPYLENE BLENDED WITH IONOMER #2

2

3

4

5

6

7

8

9

10

PARTS POLYPROPYLENE	0	25	75	100
PARTS OF IONOMER #2	100	75	25	0
MOLD SHRINKAGE, mil/in.	N/A ²	11	18	approx. 24 ³
VICAT SOFTENING POINT, °C	76	150	150	160
NOTCHED IZOD, ft-lb/in. at room temperature	6	7	1	0

11 ² Not available

12 ³ Value estimated from literature

13 This data shows low mold shrinkage and good impact
14 resistance for blends containing less than about 50%
15 polypropylene, and shows surprisingly good Vicat softening
16 point regardless of the amount of polypropylene present in
17 the blend.

18 Table 26
19 PROPERTIES OF HIGH DENSITY POLYETHYLENE BLENDED WITH IONOMER
20 #1

21

22

23

24

25

26

27

28

29

PARTS POLYETHYLENE	0	25	75	100
PARTS OF IONOMER #1	100	75	25	0
MOLD SHRINKAGE, mil/in.	6	4	22	approx. 24 ⁴
VICAT SOFTENING POINT, °C	60	82	113	160
NOTCHED IZOD, ft-lb/in. at room temperature	7	10	5	0

30 ⁴ Value estimated from literature

31 This data shows surprisingly low mold shrinkage when less
32 than about 50% high-density polyethylene is blended with
33 ionomer of this invention, and also shows surprisingly good

1 impact resistance for blends of high-density polyethylene
2 and ionomer.

3 EXAMPLE 25

4 Ethylene-alkyl acrylate copolymer blended with ionomer
5 Ethylene-methyl acrylate copolymer having 16 wt.% methyl
6 acrylate was made by the method of U.S. Ser. No. 947,870 by
7 feeding all of the methyl acrylate to a first reaction zone.
8 Ionomer of this invention was made by saponifying this
9 copolymer with aqueous sodium hydroxide by substantially the
10 method of Example 1, so that the resultant copolymer had an
11 extent of saponification of about 63%. A blend of 10 parts
12 of ethylene-methyl acrylate copolymer having 20 wt.% methyl
13 acrylate and 2 melt index and 90 parts of the ionomer was
14 made by the method of Example 24. Properties listed in
15 Table 27 were observed:
16

Table 27

	IONOMER OF THIS EXAMPLE	BLEND OF THIS EXAMPLE	ETHYLENE- METHYL ACRYLATE COPOLYMER
HAZE, %	0.5	0.6	15
60° GLOSS	151	150	70
HOT TACK: ⁵			
80°C	0.13	0.5	1.4 ⁶
85°C	0.13	1.1	---
90°C	0.18	2.2	---
95°C	1.7	2.1	---
100°C	1.9	2.3	---
105°C	2.0	2.4	---
110°C	2.0	2.1	---
115°C	2.5	2.3	---
120°C	2.6	2.4	---
125°C	2.2	2.2	---

1 extruder to react the ionomer with terminal amine and/or
2 carboxyl groups on the nylon. The reacted blend is
3 devolatilized in a devolatilization section of the reactive
4 extruder. The resultant polymer is expected to have better
5 room and low temperature impact resistance and better
6 scratch resistance.

7 Optionally, melted reacted blend, before or after
8 devolatilization, is contacted in a second reaction zone
9 with an amount of 50% aqueous NaOH that is sufficient to
10 neutralize at least a portion of the acidity on the ionomer
11 portion of the reacted polymer. This mixture is
12 devolatilized in a devolatilization zone of a reactive
13 extruder.

14 EXAMPLE 27

15 Reactive blending of ethylene-methyl acrylate copolymer with 16 ionomer

17 80 parts by weight of ionomer of Example 1 is melt-blended
18 in a twin-screw reactive extruder with 20 parts by weight of
19 ethylene-methyl acrylate copolymer having 20 wt.% methyl
20 acrylate and a melt index of 2. 0.02 part by weight
21 tetraethyl titanate is added directly to a first reaction
22 zone of the twin-screw reactive extruder to transesterify
23 the ionomer and the ethylene-methyl acrylate copolymer. The
24 reacted blend is devolatilized in a devolatilization section
25 of the reactive extruder. The resultant polymer is expected
26 to have improved tear resistance and reduced stiffness.

27 EXAMPLE 28

28 Reactive blending of ethylene-methyl acrylate copolymer with 29 ionomer

30 20 parts by weight of ionomer of Example 1 is melt-blended
31 in a twin-screw reactive extruder with 80 parts by weight of
32 ethylene-methyl acrylate copolymer having 20 wt.% methyl

1 acrylate and a melt index of 2. 0.02 part by weight
2 tetraethyl titanate is added directly to a first reaction
3 zone of the twin-screw reactive extruder to transesterify
4 the ionomer and the ethylene-methyl acrylate copolymer. The
5 reacted blend is devolatilized in a devolatilization section
6 of the reactive extruder. The resultant polymer is expected
7 to have increased scratch resistance, greater stiffness, and
8 improved tensile properties.

1 WE CLAIM:

- 2 1. A composition comprising a copolymer of alpha-olefins
3 having from two to eight carbon atoms, esters of alpha,
4 beta-ethylenically-unsaturated carboxylic acids having
5 from four to twenty-two carbon atoms, and metal salts
6 of acrylic or methacrylic acid, wherein said copolymer
7 has a haze of no more than ten percent as measured by
8 ASTM method D 1003.
- 9 2. The composition of claim 1 having a haze of no more
10 than seven percent.
- 11 3. The composition of claim 2 having a haze of no more
12 than five percent.
- 13 4. The composition of claim 3 having a haze of no more
14 than two percent.
- 15 5. The composition of claim 1 wherein the alpha-olefin
16 consists essentially of ethylene.
- 17 6. The composition of claim 1 wherein the metal of said
18 metal salt is selected from the group consisting of
19 sodium, lithium, and potassium.
- 20 7. The composition of claim 1 wherein said ester comprises
21 methyl acrylate.
- 22 8. The composition of claim 7 wherein the metal of said
23 metal salt consists essentially of sodium.
- 24 9. The composition of claim 8 wherein said metal salt of
25 acrylic or methacrylic acid comprises between about 1.9
26 and about 7.5 mole percent of said copolymer.

- 1 10. The composition of claim 9 wherein said esters of
2 alpha, beta-ethylenically-unsaturated carboxylic acid
3 comprise between about 2.3 and about 7.4 mole percent
4 of said copolymer.
- 5 11. The composition of claim 9 wherein said alkali metal
6 salt of alpha, beta-ethylenically-unsaturated
7 carboxylic acid comprises between about 3.0 and about
8 6.5 mole percent of said copolymer.
- 9 12. The composition of claim 11 wherein said esters of
10 alpha, beta-ethylenically-unsaturated carboxylic acid
11 comprise between about 2.8 and about 6.3 mole percent
12 of said copolymer.
- 13 13. The composition of claim 1 wherein the composition is
14 acidified.
- 15 14. The composition of claim 13 wherein the acid is a
16 polymeric acid.
- 17 15. The composition of claim 13 wherein the acid is
18 phosphoric acid.
- 19 16. The composition of claim 1 wherein the composition has
20 a 60° gloss of at least 100.
- 21 17. The composition of claim 1 wherein a strand, pellet, or
22 film of the composition is acidified on its surface.
- 23 18. A composition produced by the process comprising:
24 A) contacting:
25 (1) a Group IA metal-containing solution with
26 (2) a molten or fluid copolymer comprising alpha-
27 olefins having from two to eight carbon atoms

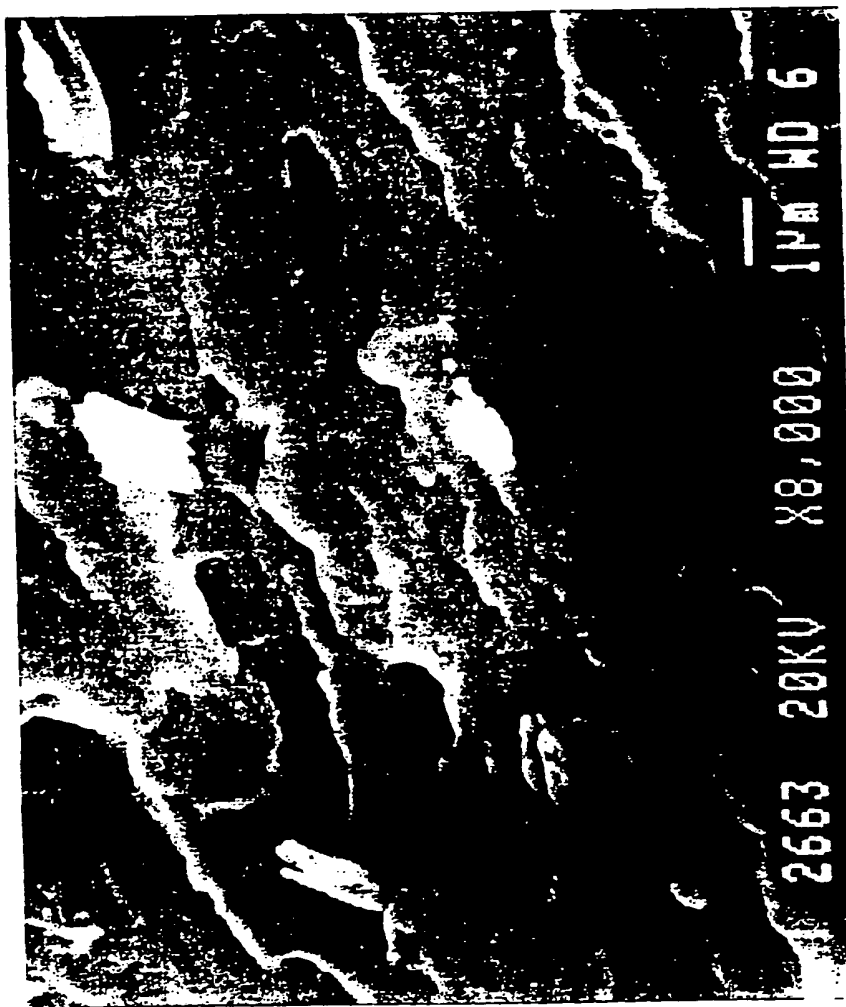
- 1 and esters of alpha, beta-ethylenically-
2 unsaturated carboxylic acids having from four
3 to twenty two carbon atoms and having a melt
4 index between about 100 and about 2000 g/10
5 min., as measured by ASTM method D 1239 at
6 190°C; and
7 B) intensively mixing the copolymer and Group IA
8 metal-containing solution at a temperature and to
9 an extent which provides an ionomer composition
10 having no more than ten percent haze.
- 11 19. The composition of claim 18 wherein said copolymer
12 comprises ethylene methyl acrylate copolymer.
- 13 20. The composition of claim 19 wherein said copolymer has
14 a melt index between 300 and 600 g/10 min.
- 15 21. The composition of claim 18 wherein the Group IA metal-
16 containing solution used to make the composition
17 comprises aqueous metal hydroxide, where the metal is
18 selected from the group consisting of sodium and
19 potassium.
- 20 22. The composition of claim 21 wherein the concentration
21 of metal hydroxide in the aqueous metal hydroxide used
22 to make the composition is at least 50 percent by
23 weight.
- 24 23. The composition of claim 18 wherein the intensive
25 mixing in the process used to make the composition is
26 provided by a twin-screw extruder.
- 27 24. The composition of claim 18 wherein the intensive
28 mixing in the process used to make the composition
29 occurs at a temperature between 200 and 350°C.

- 1 25. The composition of claim 24 wherein the temperature in
2 the process used to make the composition is between
3 about 275 and about 350°C.
- 4 26. The composition of claim 18 wherein the ionomer
5 composition is substantially free of ionic clusters
6 greater than 0.05 micron in size.
- 7 27. A film comprising the composition of claim 1.
- 8 28. The film of claim 27 wherein said film comprises at
9 least two layers, a first layer selected from the group
10 consisting of polypropylene, polyethylene,
11 polyethylene, linear low density polyethylene, and
12 nylon and a second layer comprising the composition of
13 claim 1.
- 14 29. The film of claim 27 wherein said film has a thickness
15 of no more than about 1 mil.
- 16 30. The film of claim 29 wherein said film has a thickness
17 of no more than about 0.5 mil.
- 18 31. A blow-molded article comprising the composition of
19 claim 1.
- 20 32. An easy-open package comprising the composition of
21 claim 1.
- 22 33. A composition comprising a blend of the composition of
23 claim 1 and a polymer selected from the group
24 consisting of ethylene-alkyl acrylate copolymer,
25 polypropylene, and high-density polyethylene.

- 1 34. A composition comprising the product of reacting (a)
2 the composition of claim 1 and (b) a polymer selected
3 from the group consisting of polyester, polyamide,
4 polyurethane, and polycarbonate in the presence of
5 sufficient acid to cross-link (a) and (b).
- 6 35. The composition of claim 34 wherein the reaction occurs
7 in an extruder.
- 8 36. A composition comprising the product of
9 transesterifying (a) the composition of claim 1 and (b)
10 a polymer selected from the group consisting of
11 ethylene alkyl acrylate copolymer, ethylene alkyl
12 methacrylate copolymer, polyester, polyamide,
13 polyurethane, and polycarbonate under
14 transesterification conditions sufficient to cross-link
15 (a) and (b).
- 16 37. The composition of claim 36 wherein the reaction occurs
17 in an extruder.

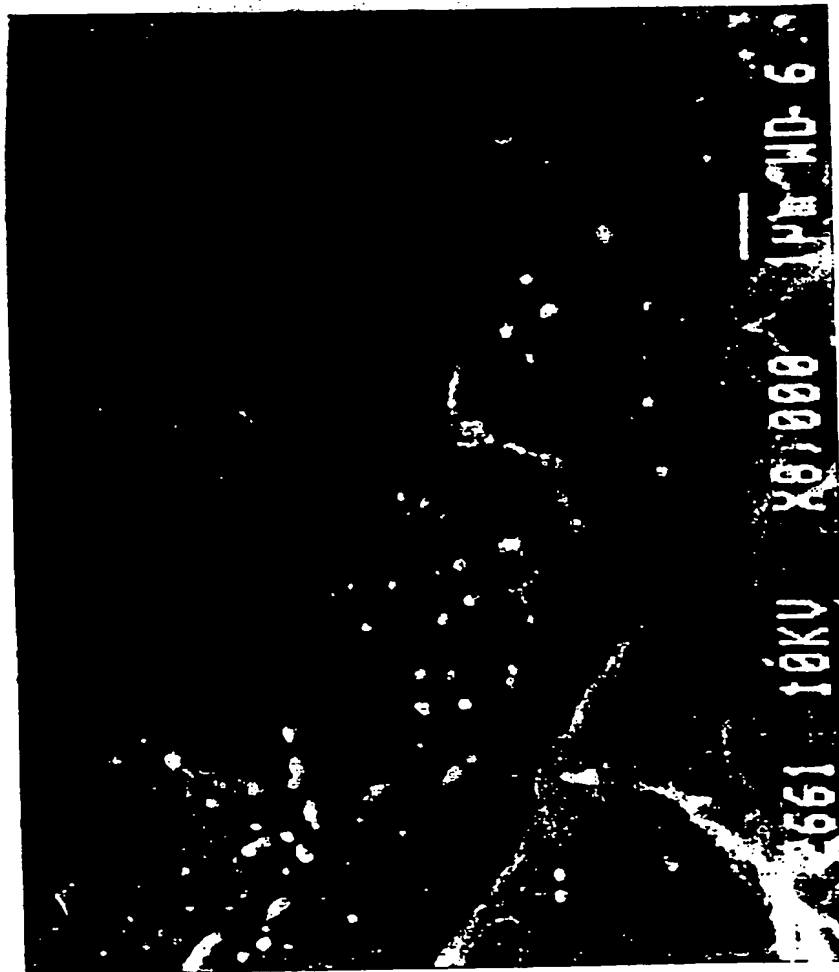
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FIGURE 1



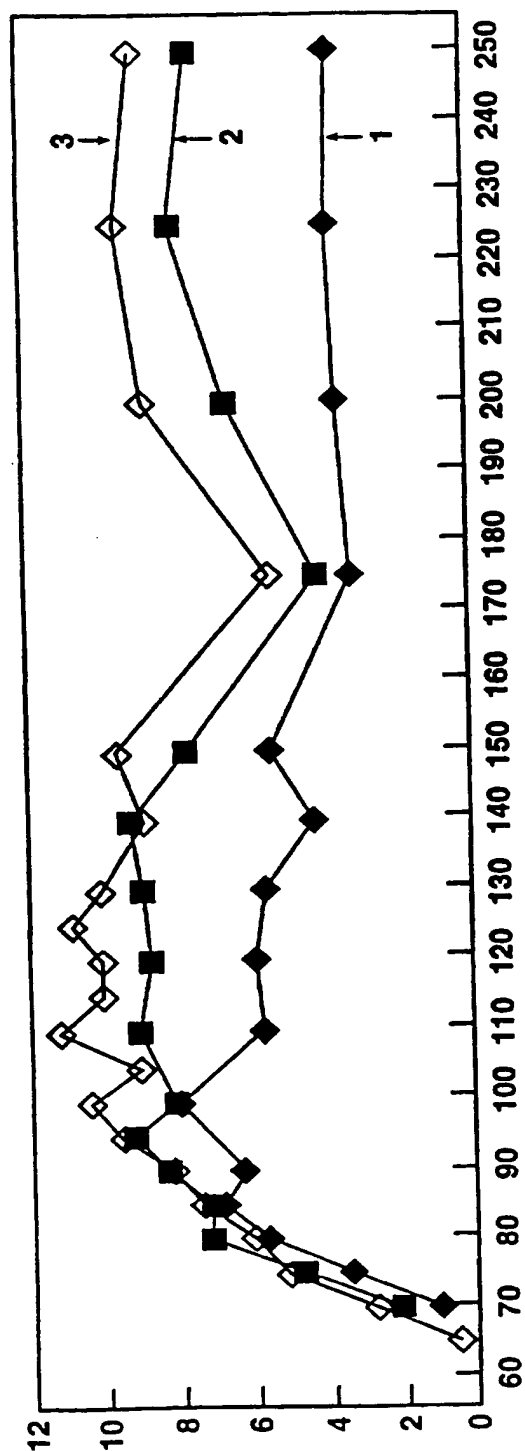
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FIGURE 2



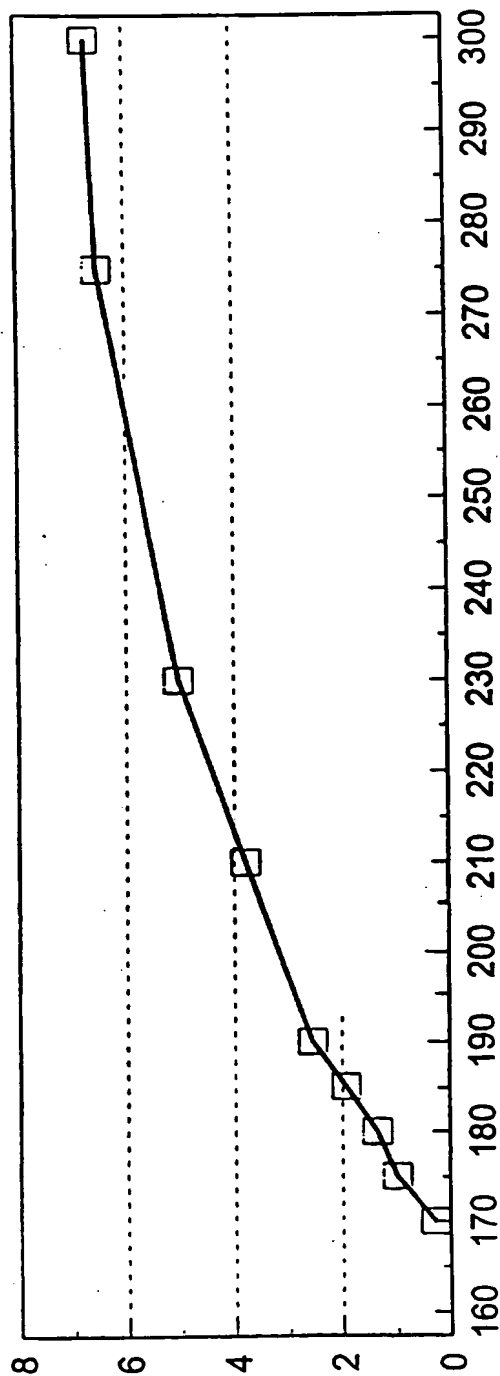
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FIGURE 3



4/4

FIGURE 4



INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/US 96/01130

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F210/02 C08F8/44 C08F8/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO,A,93 01219 (CHEVRON RESEARCH AND TECHNOLOGY COMPANY) 21 January 1993 cited in the application see page 7, line 23 - page 9, line 16 see page 9, line 24 - line 34 see page 10, line 1 - page 11, line 4; claims 1-15 ---	1-37
Y	WO,A,93 06137 (CHEVRON RESEARCH AND TECHNOLOGY COMPANY) 1 April 1993 cited in the application see page 29, line 17 - page 33, line 18; claims 1-24,28-50 ---	1-37
Y	DE,A,40 20 441 (HOECHST AG) 2 January 1992 see page 3, line 28 - line 34; claims 1-9 ---	1-37
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

24 May 1996

Date of mailing of the international search report

12 06 96

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Permentier, W

INTERNATIONAL SEARCH REPORT

Intern. Application No.
PCT/US 96/01130

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 349 828 (BASF AG) 10 January 1990 cited in the application see page 2, line 33 - line 54; claims 1-8 ---	1
A	DATABASE WPI Section Ch, Week 9548 Derwent Publications Ltd., London, GB; Class A17, AN 93-088743 XP002003889 & JP,A,05 032 798 (SHINETSU POLYMER CO) , 9 February 1993 see abstract ---	1
A	DE,A,42 35 621 (BASF AG) 6 May 1993 see claims 1-4 ---	1
A	FR,A,2 304 624 (SUMITOMO CHEMICAL COMPANY, LTD.) 15 October 1976 cited in the application see page 5, line 7 - page 6, line 10; claims 1-6 ---	1,27,28
A	CHEMICAL ABSTRACTS, vol. 101, no. 18, October 1984 Columbus, Ohio, US; abstract no. 152575h, "ION-CROSSLINKED ETHYLENE COPOLYMERS" page 16; column 2; XP002003888 see abstract & JP,A,59 102 901 (NIPPON PETROCHEMICALS CO., LTD.) 14 June 1984 ---	1
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International Application No
PCT/US 96/01130

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